Nickel and Vanadyl Porphyrins on Arabian Heavy Crude Oil

by

Adnan Ahmed Al-Hajji

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
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This thesis, written by Adnan Ahmed Al-Hajji under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CHEMISTRY.

Thesis Committee

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3-9-1980

Date

بسم الله الرحمن الرحيم

Dedicated to my

BELOVED FAMILY

ACKNOWLEDGEMENT

May all praise and thanks (first and last) be to ALLAH, The Almighty, with whose gracious help it was possible to accomplish this work.

I greatly owe my success to my parents, family, and friends for thier Dua'a and encouragement.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF SCHEMES

LIST OF FIGURES

THESIS ABSTRACT

Name of Student : AL-HAJJI, ADNAN AHMED
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This study reports the isolation and characterization of nickel and vanadyl porphyrins in the residue (1000+°F) and asphaltenes from Arabian Heavy crude oil. The residue was obtained by distillation of crude oil, where as the asphaltenes were precipitated by n-heptane from the crude oil.

Several literature-reported methods and modified separation methods were tried to isolate the nickel and vanadyl porphyrins from the residue and the asphaltenes. Metalloporphyrins were first extracted from the residue with methanol. The nickel porphyrins were separated from vanadyl porphyrins by means of adsorption chromatography on silica gel and alumina using solvents of increasing polarity.

The metalloporphyrins were first soxhlet extracted from the asphaltenes by different proportions of benzene in acetonitrile. Adsorption chromatography on silica gel and alumina, using solvents of increasing polarity, was used to separate the vanadyl porphyrins. No nickel porphyrins were detected in the asphaltenes.

The chromatographic separation process was monitored by ultra violet/visible spectrophotometry. Both of the nickel and vanadyl porphyrins were identified and characterized by ultraviolet/visible spectrophotometry and mass spectrometry. Five types of homologous series of vanadyl porphyrins were identified in the residue and asphaltenes: deoxophylleoerythroetioporphyrins (DPEP), etioporphyrins (Etio), benzoDPEP, benzoEtio, and tetrahydroDPEP. Only two types of homologous series of nickel porphyrins were found in the residue: Etio and benzoDPEP.

MASTER OF SCIENCE DEGREE

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خلاصة الاطروحة

اسم الطالب : عدنان احمد الحاجي
حقل التخصص : الكيمياء
عنوان الدراسه : بورفيرينات النيكل والفانديل في الزيت العربي الثقيل
تاريخ الدرجة العلمية: يناير ١٩٩٠م

توضح هذه الدراسة فصل و تصنيف بورفيرينات النيكل والفانديل من بقايا (ثفل) واسفالتينات الزيت الخام العربي الثقيل (فوق ١٠٠٠° ف) ، تم الحصول على البقايا (الثفل) بتقطير الزيت الخام بينما تم ترسيب الأسفلتينات بواسطه الهبتان العادي من الزيت الخام .
لقد جُربت عدة طرق منشورة في المقالات العلمية وطرق معدلة لفصل بورفيرينات النيكل والفانديل من البقايا والأسفلتينات ، لقد تم استخلاص البورفيرينات المعدنيه (metalloporphyrins) أولاً من البقايا بالميثانول ثم فصلت بورفيرينات النيكل من بورفيرينات الفانديل بواسطة وسائل الأدمصاص الكروماتجرافي على سيليكا جيل (silica gel) وألومينا (alumina) بإستعمال محاليل ذات إستقطابية متزايدة ، ولقد استخلصت البورفيرينات المعدنية من الأسفلتينات بطريقة الأستخلاص السوكسيليتي (Soxhlet extraction) بإستعمال نسب متزايدة من البنزين في الأسيتونيتريل، ثم استعملت محاليل ذات إستقطابية متزايدة لفصل بورفيرينات الفانديل بواسطة وسائل الأدمصاص الكروماتجرافي ، ولم يُعثر على بورفيرينات النيكل في الأسفلتينات .
وعلى التوالي أُخضعت عمليات الفصل الكروماتوجرافي للأشعة فوق البنفسجية والطيفية المرئية وكذالك مطياف الكتلة حيث تم تعريف وتصنيف كلٍ من بورفيرينات النيكل والفانديل في البقايا والأسفلتينات، ولقد عرفت خمسة انواع ذات السلسلة المتجانسة من بورفيرينات الفانديل في البقايا والأسفلتينات وهي: بورفيرينات ديواكسوفليوإيرثروإتيو [deoxophylloerythroetioporphyrins] (DPEP)، بورفيرينات إتيو [etioporphyrins] (ETIO) ، و بنزو أل DPEP ، و بنزو أل إيتيو مع تيتراهيدرو أل DPEP ، كما وُجد نوعان من بورفيرينات النيكل ذات السلسلة المتجانسة في البقايا وهما بورفيرينات الإتيو (ETIO) و بنزو أل DPEP .

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CHAPTER 1

INTRODUCTION

1.1- General Introduction:

The diminishing supplies of light crude oils and the daily increase in energy requirements have caused a world-wide shift to the utilization of the heavier crude oils and/or residua. Such feedstocks are becoming important to world economics as alternatives for the conversion of the "bottom - of the - barrel." The processing of these heavy feedstocks is, however, difficult due to the presence of higher concentrations of heteroatomic compounds. Furthermore, their processing is more environmentally hazardous.

Catalytic cracking and hydrocracking are the two most widely used processes. The refining of the residua using these processes is complicated by the presence of metallic organic compounds which decompose during the processing and deposit their inorganic constituents on the catalyst. The deleterious effects of the deposited metals on cracking and hydrogenation catalysts are well known. The efficient utilization of petroleum heavy ends depends on the understanding of the chemistry of their metals and metal-containing compounds contents. This requires detailed structural characterization of these compounds that are present in petroleum. Furthermore, the identification of these metal species in crude oils is of fundamental interest not only in the upgrading of petroleum but also in

understanding of the geochemical origins of petroleum sources. The nature of these metal species in crude oils is important to those engaged in petroleum exploration, production, and refining . This understanding, for example, helps refining chemists seeking to minimize catalytic poisoning during residue upgrading.

Nearly half of the elements in the periodic table have been identified as trace elements in crude oils. Among these metals the most abundant and undesirable are vanadium and nickel. Depending on the origin of the crude oil, the concentration of the vanadium varies from as low as 0.1 ppm to as high as 1200 ppm, while that of nickel commonly varies from trace to 150 ppm. Vanadium and nickel are thought to occur in petroleum in two forms: porphyrinic and nonporphyrinic. Little is known about the nature of the nonporphyrins. However, the porphyrins have been extensively studied not only because of their deleterious effects but also for thier considerable role as geochemical markers.

1.2- Need for the Study:

Porphyrins and metalloporphyrins have been noted in various branches of science and industry. Their presence in crude oil is important not only from scientific point of view but also from both of the economic and environmental stand points. Therefore, considerable attention has been focused on vanadyl- and nickel porphyrins in crude oils to understand their nature and effects.

Porphyrins and metalloporphyrins have become a hot subject in

petroleum industry. Their identifications in petroleum oil and shales has provided a convincing evidence that petroleum is derived from a biogenic source. Since porphyrins and metalloporphyrins (refered to as petroporphyrins due to their difference from the naturally occuring porphyrins according to Crowin (1)) are thermally stable in the geosphere, it is reasonable to assume that these metalloporphyrins of a source rock leaves an imprint in its derived crude oils which might not have altered significantly during the migration of the crude oil to its reservoir. Therefore it may be possible to establish (a) an understanding of the origin of the crude oil, (b) the diagenetic and the catagenetic pathways in the oil formation, and (c) maturation, correlation, depositional and environmental reconstruction studies. Such studies are extensively reported in the literature (e.g. 2,3).

There are, however, disadvantages resulting from the presence of these metalloporphyrins in petroleum. As a result, it is difficult to upgrade the heavy petroleum residue because of the large concentration of the metals, mainly vanadium and nickel which are complexed in porphyrins. The metallopetroporphyrins that are present in petroleum are basic stabilizers of petroleum emulsions and , thus, hinder their demulsification (4). Metalloporphyrin complexes affect the stability of the furnace fuels due to their nitrogen and metal complexes. These compounds are remarkably stable and, thus, cannot be removed from petroleum stocks by usual acid treatment used to remove inorganic salts and basic nitrogen compounds (5).

Vanadium and nickel seriously affect cracking catalysts when they

accumulate on the particles of the catalyst over time. The deleterious effect of the nickel lies in its enhancement of undesirable reactions due to excessive yield of coke and hydrogen. Where as vanadium deposit causes alteration in the catalyst structure (6). In addition, the two metals poison and reduce the life time of the catalyst employed in the process of hydrodesulfurization. This is caused primiraly by the irreversible adsorption of these metals on the pores of the catalyst which prevents access to the active site of the catalyst due to their blockage (5). It has been found that nitrogenous compounds cause copious sludge formation in furnace oils (7). Also, small amounts of nickel and vanadium accumulating from chargestocks poison clay and synthetic cracking catalysts.

Vanadium and nickel are undesirable when present in residual fractions used as fuel because of thier tendency to cause corrosion and pitting of materials of constructions with which they come in contact. For example, vanadium, if present in residual fuel oils, causes corrosion and fouling of high temperature boilers and the blades and heat exchanger's tubes of the gas turbines (6). Vanadyl porphyrins have been shown to catalyze asphalt oxidation which causes failure in roofing and the paving of highways (6).

During combustions of heavy fuels, large amount of vanadium-containing compounds are discharged into the atmosphere via flue gases. This causes a serious health problem as far as the environmental protection is concerned (4). In addition, vanadium and nickel that are found in petroleum are toxic. They affect the operations that are designed to remove the sulfur and nitrogen

which are two primary air pollutants from petroleum (6).

The deleterious effects of these metals to petroleum processing equipments is minimized if these compounds are demetallized (4).

1.3- Current Status:

Rankel studied the decomposition of the Arabian Heavy crude oil (8). The total petroporphyrins were extracted by demetallation with methane sulfonic acid from the Arabian Heavy crude oil before and after it was subjected to the process condition of heat, air, hydrogen, or hydrogen sulfide. The extracted petroporphyrins were measured spectrophotometrically. It was found that more than 90% of the petroporphyrins from Arabian Heavy crude oil decompose to polypyrrolics at 240 °C in 24 hours, and more than 95% degrades on V_2O_5 catalyst in half an hour. It was concluded that petroporphyrins decompose if subjected to thermal treatment and/or a mixture of reactive gases viz. H_2 and H_2S.

HajIbrahim studied the HPLC fingerprinting of free-base petroporphyrins of different crudes (9). Saudi Arabian Safaniya crude was one of these crudes. He was able to detect up to seventeen different peaks. He did not provide identification of the metallopetroporphyrins present in the Arabian Heavy oil. The aim of his study was to assess the applicability of HPLC fingerprinting to selected crude oils.

The present study will focus on the methods of separation, isolation and characterization of nickel and vanadyl porphyrins in Arabian Heavy crude oil residue and asphaltenes. Electronic absorption (UV/Vis) spectrophotometry and mass spectrometry will be used for characterization. High performance liquid chromatography will be used for fingerprinting purposes.

CHAPTER 2

LITERATURE REVIEW

2.1- Types of Porphyrins Present in the Geosphere:

The metalloporphyrins were the first compounds claimed to be of conclusive biological origins. Treibs discovered in the year 1934 that a wide variety of petroleum and bitumen contain porphyrins (10). Since his discovery, researchers continued to look for such complex compounds in a variety of samples of different geological origins. In the early days of the study of porphyrins in geospheres, the complexity of these pigments was not known. With the advent of mass spectrometry, electronic absorption spectrophotometry, infrared spectroscopy, NMR, and ESR, a lot of the complex heterogeneity of the porphyrins have been resolved.

Four main types of porphyrins along with their homologs have been reported in the literature to be present in petroleum and bitumen. These are deoxophylleoerythroetioporphyrin (DPEP), etioporphyrins (Etio), benzo DPEP and benzo etioporphyrins and benzoporphyrins (Benzo). Baker and Louda (3) have presented the different types of the porphyrins and metalloporphyrins found in the geosphere along with their structures and their precursors. Also, Chicarelli et al. (11) have summerized the occurrence of sedimentary porphyrins whose structures have been fully or partially established. Types of these porphyrins and their structures are also listed.

Biogenic origins of such compounds were discussed as well.

2.2- Geochemistry of Porphyrins:

Petroporphyrins are claimed to be traceable artifacts of living systems from as old as billions of years of accumulations and depositions. Since their discovery by Treibs in 1934 (10), the geochemical evolution of these porphyrins is still incompletely understood. A series of reactions has been postulated by Treibs to account for the transformation of the chlorophyll of the green plants, the starting material, to the end product found in petroleum, metalloporphyrins. Based on his observation, a new concept, biological markers, has been put forward to explain the geochemical evolution processes and to understand the complexity of such compounds. Geoporphyrins are being used as correlation parameters for oil-oil and oil-source rock as well as a parameter to reconstruct the environmental deposition. The geochemistry of porphyrins has been widely studied and reviewed in the literature. Filby and Berkel (12) surveyed the geochemistry of metalloporphyrins in fossil fuels. Also, Baker et al. (13) have discussed the geochemistry of porphyrins. Baker and Louda (3) have reviewed in much details the geochemistry of porphyrins.

2.3- Separation Methods:

The porphyrins in petroleum are present predominantly as vanadyl and/or nickel chelated compounds. These compounds are very similar to material with which they are associated in many of their physical properties. Therefore, there is no single procedure used for the isolation of the porphyrin complexes from their host materials. There are many isolation and purification methods reported in the literature. Generally, the methods can be classified into three types: acid demetallation, liquid extraction, and chromatography. Quirke (14) has reviewed those methods that have general applications to the analysis of the geoporphyrin mixture. Also Baker el al.(13) gave a good summary of the methods of isolation, fractionation, and purification of the geoporphyrins. They also provided a comparison of these methods, their field of application as well as their efficiency.

2.3.1- Liquid Chromatography:

The liquid chromatography provides the major advantage of being gentle with the sample and systematic multi-dimensional separations are easier to be obtained.

Freeman et al. (15) reported for the first time the use of the medium performance liquid chromatography (MPLC) for group isolation of geoporphyrins from crude oil, oil sand bitumen, and shale extract. The MPLC apparatus consisted of a glass column, 5 or 10 cm in length, with endfittings, a visible light monitor, nitrogen gas at 1-2 psi to pressurize the carrier solvent

through the column and a flow velocity of 3 to 5 cm/min through the column. This apparatus was found to be able to separate the geoporphyrins into three fractions: nickle porphyrins, vanadyl porphyrins, and carboxyl metalloporphyrin sub group.

2.3.2- High Performance Liquid Chromatography:

The chromatographic methods, such as thin layer chromatography and column chromatography which are frequently used to separate porphyrins and metalloporphyrins from geological sample, were time consuming, laborious and afforded insufficient separation. This makes them practically not suitable for structure elucidation and correlation studies. High performance liquid chromatography (HPLC) offers a greater resolving power than the other chromatographic methods. It can also be a straightforward separation method for microquantities of a complex mixture of porphyrins. Furthermore, it can be employed for identification of individual porphyrin.

HajIbrahim et al. (16) applied high performance chromatography in the analysis of geological porphyrins and carotenoid. Irregular silica gel particles (5-μ) packed column with linear gradient elution of 2-50% chloroform in hexane at 1.8 ml/min. over 20 min. was used to separate mixture of petroporphyrins obtained from Boscan crude oil by liquid extraction and then demetallization. The chromatographic behavior of the petroporphyrins was assayed by taking UV/Vis and MS measurements of samples collected from HPLC column. Separation according to structure type was observed using standard porphyrins. The order of elution was detected to be Etio followed by

DPEP and then rhodo. Also, complex mixtures of nickel- and vanadyl porphyrins obtained from Boscan crude were shown to be separated from each other by HPLC.

HajIbrahim (17) has developed a high performance liquid chromatography method for the fractionation and fingerprinting of petroporphyrin mixtures from Boscan crude oil. The method involved the fractionation of the demetallated porphyrins on silica columns followed by rechromatography of the trapped fractions on C18 columns. This method was reported to be fast and effective for fingerprinting of porphyrins as well as for isomers separation. The mobile phase used was toluene in hexane (1:9 v/v) as solvent A and toluene/chloroform (1:1) as solvent B. gradient elution of 20% A to 100% B over 40 min at a flow rate of 1.5 ml/min was employed in case of the silica column. Isocratic elution of water in acetonitrile (3:17 v/v) was used in the case of the C18 column. The carbon number of the peaks were assigned by coinjection with previousl characterized porphyrins.

HajIbrahim used HPLC for fingerprinting of crude oils for pollution control purposes (9). Total demetallated porphyrins from "export" and "weathered" crude oils obtained from Kuwait (Burgan), Saudi Arabia (Safaniya), North Sea, Alberta, (Athabasca tar and Bellshill Lake oil) and Venezuela, (Boscan) were studied. The purpose of the study was to see the effect of the weathering process on the distribution of these porphyrin compounds and to assess the applicability of the HPLC in this regard. The study revealed that weathering had no effect on the distribution of the

porphyrins and thus it was concluded that they are not readily susceptible to natural weathering processes.

Eglinton et al. (18) used HPLC coinjecting data along with mass spectrometry and ^{1}H NMR to determine the structure of the petroporphyrins separated by a variety of chromatographic procedures and finally demetallization from Gilsonite of Uinta Basin, Utah. U.S.A. Also they have employed HPLC technique to perform fingerprinting of demetallated porphyrins separated from different oils from Venezuela and California, U.S.A.. It was concluded that different oils from Boscan, Venezuela, had the same HPLC patterns suggesting the same origin. The HPLC fingerprints of the porphyrins from California were different. Thus, HPLC was observed to be capable of being used for correlation studies.

Mozzhelina et al. (19)used reverse phase HPLC to analyze the vanadyl porphyrins of different oils from West Siberia and Sakhalin. The samples examined were observed to consist of several compounds having different retention times. It was also observed that as the chromatographic mobility of the vanadyl porphyrin fractions increases, the number of the homologous series in them and their average molar mass increase. Therefore, it was concluded that high molar mass porphyrin fractions can not be separated by reverse phase column chromatography. It was also observed, using authentic vanadyl porphyrin compounds, that the substituent distribution in the porphyrin ring influences considerably the chromatographic behaviour of the particular porphyrins. Comparison of the retention times of individual

petroleum vanadyl porphyrins with their molecular weights indicated that the retention times of the porphyrins of Etio type within individual compound groups were determined by the number of the carbon atoms in lateral chain of the porphyrin ring. Thus, it was claimed that as the aliphatic component of the compounds increases, the retention time increases. In addition, it was seen that compounds with odd number of methylene groups were more strongly retained on the reverse phase column than porphyrins with even numbers. DPEP porphyrins were observed to be strongly retained on such a column than their Etio counterparts. However, DPEP with odd number methylene groups in the lateral ring was indicated to be more retained than those having even number of methylene groups.

Shul'Ga et al. (20) examined the vanadyl porphyrins from West Surgut, U.S.S.R. which was separated into seven fractions by preparative TLC and by reverse phase HPLC. Several peaks were detected for each fraction indicating the presence of both of homologous series of DPEP- and Etio- vanadyl porphyrins as assayed by coinjection of known compounds and MS data.

Ekstrom et al. (21) employed reverse phase HPLC to separate the mixture of the vanadyl porphyrins obtained from Julia Creek deposit into seven fractions. The fractions were collected as they eluted from the column and then analyzed by MS.

Mozzhelina et al. separated the vanadyl porphyrins obtained from crude oils of different deposits in the U.S.S.R. by means of reverse phase HPLC (22). The separated porphyrins were indicated to consist of homologues with

different isomeric composition and various molar masses.

Shilonosova et al. (23) used preparative reverse phase HPLC for further separation of vanadyl porphyrins (obtained from crude oil and vacuum gas oil from mixed Siberian crude) after they were separated on TLC. Each peak was collected and analyzed by MS to determine the molecular mass composition. It was found that each peak with different retention time and peak intensity had a specific molecular mass.

Sundararaman et al. (24) used the reverse phase HPLC to determine the fingerprinting of the vanadyl porphyrins separated from Boscan crude oil before and after lab. simulation pyrolysis. This was to determine the DPEP/Etio ratio in order to evaluate the maturation effect on the amount of the etioporphyrins.

Quirke et al. (25) analyzed the nickel, vanadyl, and free base porphyrins from sediments of Legs (Angola Basin) by preparative high performance liquid chromatography. The separated peaks were assessed by mass spectrometry.

Sundararaman (26) described a rapid highly reproducible high performance chromatographic method for the analysis of vanadyl porphyrins from Boscan oil. Structural and isomeric porphyrins corresponding to homologous series of DPEP and Etio have been observed from the liquid chromatogram. The Etio types were generally observed to elute before the DPEP type.

Spencer et al. employed normal phase HPLC for removal of vanadyl porphyrins (27). They used programmed gradient solvent elution of 9:1 hexane/toluene as a weak solvent and 1:1 chloroform/toluene as a strong solvent. Partially resolved overlapping peaks of Etio as the first eluent and DPEP as the second eluent were observed. It was also suggested, from the HPLC chromatograms, that the short chain Etio species were prevailing since the Etio type concentration has gradually increased on going from nonpolar to polar eluents.

Barwise (28) used HPLC data to derive the ratio of Etio/(Etio+DPEP) in order to study the mechanisms involved in altering DPEP-Etio ratios in sediments and oils. The source rocks studied were from the Gulf of Suez formation. Three columns of Spherisorb silica linked in series and spectrophotometer set at 400 nm for detection were used. A parameter called the porphyrin index was constructed from the HPLC measurement of the demetallated porphyrins to reflect the Etio/(Etio+DPEP) ratio. It has been found that the ratio was affected by the thermal maturity factor; there was a decrease in the value as the depth, at which the sample was taken, increased. The Etio and DPEP vanadyl porphyrins concentrations obtained from HPLC measurement were calculated and expressed in μg porphyrins per total carbon in the sediment. It has been noted that etioporphyrin were present in every sediments, suggesting that etioporphyrins must have been derived from low temperature diagenetic processes. A sudden increase in the concentration of the Etio type was noticed on the onset of the generation of oil from the source rock which could imply that the Etio type was derived from the thermal

decomposition of kerogene. In addition it was observed that at high maturity, there were little or no porphyrins which suggested the thermal decomposition of porphyrins at high temperature.

HajIbrahim et al. (29) fractionated the total petroporphyrins from Boscan crude oil, its proposed source rock and Carneros oil by preparative normal phase HPLC. These fractions were then analyzed by mass spectrometry and non-aqueous reverse phase (NARP) HPLC was used to separate the isomers. Seven Etio and three DPEP porphyrins were isolated by TLC and preparative HPLC and were shown to be mainly single-carbon-number species (one compound) by MS. Each fraction was analyzed by normal and reverse phase HPLC and confirmed by MS. The C_{30} Etio was shown by reverse phase to have a mixture of at least two isomers. It was observed (from normal phase HPLC) that the polarity of the etioporphyrins is inversely proportional to both carbon number and β -unsubstituted positions.

McFadden et al. (30) studied the petroporphyrins extracted from Boscan crude oil by the application of combined liquid chromatography/mass spectrometry (LC/MS) technique. Silica column was used for the liquid chromatography part. Ion peaks plotted were found to correspond to homologous series of petroporphyrins of DPEP and Etio.

2.3.3- Gel Permeation Chromatography:

Biggs et al. (31) studied the application of size exclusion chromatography-high performance liquid chromatography (SEC-HPLC) and reversed-phase

chromatography (RP-HPLC), with element specific detection (inductively coupled plasma and direct current plasma emission spectroscopy, ICP and DCP) to selected crude oils for fingerprinting purposes. The profile was seen to be of bimodal size distribution for the vanadium compounds.

Sundararaman et al. (24) reported the molecular size profile of vanadium containing components of Boscon asphaltenes separated by size exclusion chromatography and detected by specific element monitoring ICP. The profile showed a resolved peak for vanadyl porphyrins and the remainder of the profile corresponded to non-porphyrin vanadium compounds. Also SEC was used to separate vanadyl porphyrins from the asphaltenes of Boscan crude which were monitored later by UV/Vis absorption spectrophotometry.

Blumer and Synder separated the porphyrins of the Triassic oil shales of Serpiano (Switzerland) by gel permeation chromatography on alkylated Sephadex (LH-20) and Styragel columns(32). The porphyrin eluents were detected by UV/Vis absorption at 410 nm and MS. Homologous series of porphyrins pigments extending into the high molecular weight region ($>$ 20,000 mol. wt.) were observed. It was believed that these pigments were the products of heterogeneous polymerization of porphyrins derived from biological sources with the bulk organic matter of the sediment.

Blumer and Rudrum (33) separated vanadyl porphyrin complexes of approximately 1100 molecular weight from Triassic and a Pennsylvanian oil shale by gel permeation chromatography (GPC). The GPC column was of Sephadex LH-20. The sample was eluted with 1:1 benzene/methanol. The

light absorption of porphyrin was detected at the breakthrough volume. Effective separation of homologous series according to molecular weight was shown to take place.

Šebor (34) used adsorption chromatography and gel premeation liquid chromatography (GPC) to separate nickel- and vanadyl porphyrins from a rock extract taken from a vicinity of an oil deposit in the Gulf area. The GPC behavior of the isolated fractions from the GPC column was analyzed by MS. The GPC separation was performed on the metalloporphyrins, which were separated by the adsorption chromatography, using a column packed with a styrene-divinylbenzene copolymer containing 3 wt% of divinylbenzene. It was observed that the vanadyl porphyrins eluted before the nickel porphyrins from the GPC column. It was, therefore, suggested that the reason for such a separation was the steric factor that has controlled the separation process to a great extent. The nickel porphyrin is planar with the nickel atom being located in the plane formed by the four pyrrole rings, while the vanadyl porphyrin has a tetragonal pyramidal geometry with the oxygen atom occupying the apex of the pyramid and the vanadyl group lying outside the tetrapyrrole plane. Thus, they conclude that the primary factor affecting the GPC behavior of both metalloporphyrins was the geometry of the nickel ion or the vanadyl ion in the metalloporphyrin molecule and to a lesser extent on the number of carbon atoms attached to the porphyrin ring.

Goulan et al. (35) employed the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES)

characterization of the vanadium chemical environment in Boscan asphaltenes. It was reported that although UV/Vis spectrophotometry was found to underestimate the amount of porphyrins in the sample because the level of porphyrin has reduced to < 15% from the 4000 ppm of metal due to the successive extractions, the quantity measured by X-ray absorption technique has indicated that EXAFS spectra of these fractions were still dominated by the typical pattern of the vanadyl porphyrins. The prepeak observed in the XANES spectra also supported the presence of considerably large amounts of porphyrins in these fractions. The problem of the underestimation of the content of porphyrins in heavy fraction by UV/Vis spectrophotometer was claimed to be due to the hardly detectable microheterogeneity of the test solutions.

2.4- Characterization Methods:

Vanadyl and nickel porphyrins are found to occur in petroleum in different types of homologous series. Thier characterization and identification are important for research and industry. Several techniques that are used for the identification and characterization are reported in the literature. Electronic absorption spectrophotometry along with mass spectrometry is widely used for identification of porphyrins. Nuclear magnetic resonance spectroscopy is becoming another frequently used technique. Infrared spectroscopy and electron spin resonance are less used in this field. High performance liquid chromatography is being utilized for fingerprinting as well as for separation of porphyrins. Crystallographic technique is applied for the

determination of the crystal structure of the porphyrins.

2.4.1- Electronic Absorption Spectrophotometry:

The electronic spectroscopy is an important tool for the analysis of petroporphyrins as well as for metallopetroporphyrins. The electronic spectra of the porphyrins can be divided into two parts: near ultraviolet (UV) and visible (Vis). The near UV band at ca. 400 nm is extremely intense and named after its discoverer, Soret. The visible part of the spectra (500-700 nm) is the most useful because it is very sensitive to structure changes and it is readily observed (36). The metalloporphyrins are characterized by two banded spectra in the visible region in addition to the Soret band at ca. 400 nm. Vanadyl porphyrins, for example, have absorption bands at ca. 405, 530, and 570 nm while nickel porphyrins have absorption peaks at ca. 390, 514, and 550 nm. The free-base porphyrins are, however, characterized by a four-banded spectra in the visible region in addition to the Soret band at ca. 400 nm. Etioporphyrins, for example, have absorptions at 399, 499, 532, 566, and 619 nm (14). It was noted earlier that the relative intensity of the four visible bands of the free-base porphyrins is sensitive to the structure of the porphyrin macrocyclic molecule. These visible bands numbered I-IV starting from the long wavelength were found to vary markedly with the substituents. Etio type has a spectrum with the four bands having relative intensity of the order of IV > III > II > I. DPEP is characterized by IV > I > II > III, while that of rhodo DPEP type is determined by III > IV > II > I (14,36). The electronic spectra of the porphyrins and metalloporphyrins have been reviewed in detail

by Baker and Palmer (13).

2.4.2- Infrared Spectroscopy:

The application of infrared (IR) spectroscopy to petroporphyrins and metallopetroporphyrins has met with some difficulties. The IR spectrum of the porphyrins is sufficiently complex that even with pure single compounds recognition of extraneous bands caused by moisture, contaminants and solvent residue is difficult. It has been noted that there has been some shifts in shape and position of bands with different sample preparative techniques (36). The main uses of IR spectra in the field are to indicate the presence or absence of a carbonyl group and a vanadyl (V=O) group. Infrared spectroscopy of porphyrins and metalloporphyrins has been thoroughly reviewed in details by Alben (37).

Erdman et al. has reported the IR spectra of copper, nickel- and vanadyl etioporphyrin I (38). Direct evidence for the vanadyl band was obtained by comparison of the IR spectra of vanadium oxytrichloride with that of the etioporphyrin I and its copper, nickel and vanadium complexes. The curves for the three metalloporphyrins were similar except for a sharp absorption band for the vanadium complex at ca. 995 cm^{-1}.

Malhotra and Buckmaster (39) used Fourier transform IR (FTIR) along with electron paramagnetic resonance (EPR) to determine various types of vanadium coordination in three different fractions of Boscan asphaltenes separated by the gel permeation chromatography (GPC). Absorption bands

were detected for the three fractions at 1003, 1001, and 999 cm^{-1} respectively. These bands were assigned to the vanadium-oxygen double band stretching mode.

Gall et al. used IR spectra to characterize the metalloporphyrins separated from Boscan crude oil (40). UV/Vis measurements were noted to give characteristic peaks for vanadyl porphyrins. This observation was supported by the vanadium-oxygen stretching vibration band at 1000 cm^{-1} as detected from the IR spectra.

Yeletskii and Vylegzhanin (41) employed UV/Vis and IR spectra to study the changes occuring in the structure of the vanadyl porphyrins from West Surgut deposit, U.S.S.R., as it was subjected to thermal oxidation. The UV/Vis measurements indicated similar spectra before and after exposure to the thermal oxidation suggesting that the porphyrin molecule still retained its electron structure. At the same time the IR spectra differ considerably after the exposure. New bands at 1725, 1270, 1070 cm^{-1}, were observed and the bands at 840 and 990 cm^{-1} disappeared. The appearance of a band at 1725 cm^{-1} in the oxidized vanadyl porphyrins indicated the appearance of a carbonyl group in the structure of the porphyrin molecule. Therefore, it was concluded that vanadyl porphyrins were oxidized to form products containing oxygen at mild condition but the porphyrin system does not break down.

Blumer and Rudrum (33) used IR spectra to study the extent of alkylation and the vanadyl content of the GPC separated fractions from a Pennsylvanian

oil shale of Triassic era. The intensity ratio of C-H/V=O was measured for the three fractions and compared.

Chakraborty and Bhatia studied the IR spectra of the vanadyl porphyrins recovered from Darius crude oil, Iran (42). A characteristic absorption band for ester carbonyl was detected at 1724 cm^{-1}.

2.4.3- Nuclear Magnetic Resonance Spectroscopy:

Nuclear magnetic resonance (NMR) spectroscopy has been generally less utilized in characterization and/or structure elucidation of porphyrins or metalloporphyrins than the UV/Vis absorption and mass spectrometry. This is due to the complexity of the spectra produced by such a technique and its sensitivity to small amounts of impurities. Extraneous materials of low molecular weight present in the amount of 1-2% with material of molecular weight of 500 or more produce a proton resonance signal equal in size to that of porphyrin. Also the presence of complex compounds of many homologous series in petroleum and bitumen renders the NMR spectra unresolvable and uninterpretable (36). However, as the separation techniques are more refined and with advent of high resolution NMR instrumentations, this technique is being applied in the field of porphyrins and metalloporphyrins. In fact NMR spectroscopy is one of the most important methods employed for the analysis of individual porphyrins. The technique only gives the number and type of substituents on the porphyrin macrocycle. Analysis of porphyrins by the use of nuclear Overhauser effect (nOe) techniques has been the method of choice

provided that all the meso (bridge) protons are fully resolved. In such cases, it is possible to assign the structure of the porphyrins by irradiating each signal in turn, and determining which of the other is enhanced by difference spectroscopy. The nOe enhancements are observed only for groups close to the irradiated one (14).

Prowse et al. (43) have determined the structure of a representativ series of C_{33} and C_{32} di DPEP porphyrins isolated from El Lajjun shale from Jordan using nOe techniques. A 400MHz NMR spectrometer was employed. This study was meant to evaluate a previous suggestion that this type of compound and sedimentary monobenzoporphyrins are related in structure and origin. The structure of the C_{33} was assigned as 13,15-ethano,-3,8-diethyl-2,7,12,18-tetramethyl-13,17-propano porphyrin. The relative positions of the substituents around the macrocycle ring (except CH_3 -2 and 18) could not be discriminated by nOe for C_{32} di-DPEP.

Chicarelli et al. (44) have used the ^1H NMR spectroscopic analysis to determine the structure of C_{31} and C_{32} alkyl porphyrins present in Serpiano oil shale as vanadyl porphyrin. These were isolated and demetallated compounds. Separation of the porphyrins to their individual compounds were achieved by preparative HPLC and then purified by TLC. The compound was chelated with zinc. The structure was determined by NMR spectroscopic analysis of the zinc complexes using selective decoupling and nOe (43). Four structural isomers of C_{32} porphyrins containing exocyclic ring were determined by NMR

to be present in Serpiano oil shale having five, six, or seven membered exocyclic ring or a methyl-substituted six membered ring. Similarly other four isomers for C_{31} were also known having five, seven, or a methyl-substituted five, or six membered ring.

Chicarelli et al. determined the structure of several alkyl porphyrins from different sources: Boscan crude oil, Serpiano shale oil and Gilsonite bitumen (11). The metalloporphyrins obtained were demetallated and separated to their individual components by preparative scale HPLC and then converted to their zinc(II) chelates and purified by TLC . The samples were then analyzed by a 400 MHz NMR Spectrometer.

The structure of C_{34} DPEP porphyrin isolated from Serpiano shale oil was determined by selective decoupling and nOe techniques. The structure was determined to be (13^1- methyl) - 13,15-ethano - 3,8-diethyl - 2,7,12,18-tetramethyl $13^2(15^2)$- enoporphyrin. The structures of C_{32} and C_{33} DPEP, isolated as free base from Gilsonite bitumen in which they occur as Ni(II) porphyrins, were determined as well. C_{32} was found to be (13^1- methyl) - 13,15-ethano - 8,17-diethyl - 2,3,7,12,18-pentamethyl porphyrin, and that of C_{33} was found to be (13^1- methyl) - 13,15-ethano - 2,4-diethyl -1,2,3,5,7,8-hexamethyl porphyrin.

Quirke et al. made use of ^1H NMR to determine the structure of Etio and DPEP porphyrins isolated chromatographically from Gilsonite bitumen, Utah, U.S.A. (25). Seven Etioporphyrins ranging from $C_{29} - C_{32}$ were isolated and

found to contain methyl, ethyl, and hydrogen substituent and no alkyl groups in the meso positions. One of the C_{29} etioporphyrin fractions was assigned unambiguously as 2-ethyl-3,7,8,12, 13,17,18-heptamethyl porphine. The presence of an isocyclic ring was confirmed in the C_{31} DPEP porphyrin fraction.

Shul'Ga et al. (20) reported the structure of the Etio and DPEP porphyrins found in West Surgut deposit as vanadyl porphyrins which was separated by HPLC and then demetallated. The NMR data were found to confirm the presence of the 5-membered isocyclic ring in the DPEP fractions.

C_{30} Etio was found to be 3,8-diethyl - 2,7,12,13,17,18-hexamethyl porphyrin. C_{32} was determined to be 13,15-ethano-3,8,17-triethyl - 2,7,12,18-tetramethyl porphyrin, while C_{31} DPEP was 13,15-ethano - 8,17-diethyl - 2,3,7,12,18-pentamethyl porphyrin. C_{30} DPEP was found to be 13,15-ethano -3,8-diethyl - 2,7,12,18-tetramethyl porphyrin.

Chakraborty and Bhatia used NMR to study the vanadyl porphyrins separated by TLC after they were recovered from Darius crude oil, Iran, by successive column chromatographic processes (42). Assignments of ^1H NMR of all the protons indicated the similarity of the three fractions.

2.4.4- Electron Spin Resonance:

The vanadyl ion $(V=O)^{2+}$ has a long relaxation time and, consequently, has been extensively studied by electron spin resonance (ESR). Since almost

all the vanadium found in petroleum exists in the +4 oxidation state, the hyperfine structure of $^{51}V^{4+}$ can furnish a quick determination of the vanadyl content by ESR and thus could be used for qualitative as well as for quantitative determination of the concentration of the vanadium in a sample.

Nasirov et al. (45) have determined the vanadyl porphyrin complexes in certain crude oils of Western Kazakhstan by means of ESR. The ESR spectra were taken at a range of temperature from -190°C to +130°C. The parameters of the spin-Hamiltonian A_{II} and A_{I} were determined from the spectra of one of the sample and found to be in good agreement with the constant of the spin-Hamiltonian of VO^{2+} porphyrin complexes reported in the literature. By comparing the signal intensities of the standard and the crude oil/toluene solution, the concentration of vanadium in the crude oil was interpolated.

Dickson and Petrakis (46) extended the use of ESR by obtaining precise g_o values for separated fractions from petroleum of East Mara to support the interpretation of the observed differences in ESR g_o values with those obtained by electronic (visible region) spectra. It was proposed that the differences in ESR parameters can represent structural differences in the ligand distribution around the vanadyl in the vanadium complex. It was concluded that the difference in the ESR g_o values, when characterizing vanadium in petroleum, do have significance in terms of non-porphyrin identification since the Δg_o value of the nonporphyrin vanadium complex indicated a shift from that of the porphyrinic vanadium complex.

Malhotra and Buckmaster used high precession 34 GHz EPR to study the coordination of vanadyl complexes in various asphaltene samples from Canada, USA, and Venezuela (47). Spin Hamiltonian parameters, g and A were used to classify asphaltenes into those with nearly identical g and A values to those for the vanadyl tetraphenyl porphyrins doped in carbonaceuos materials and those for which these parameters were identical to those for the vanadyl etioporphyrins. Quantitative statistical analysis using model compounds with coordination N_4, N_2S_2, NS_3, S_4, S_2O_2, and O_4 were found to show that these parameters could not be used to predict the coordination of various asphaltenes. However, it was found that g_o was a better parameter than A_o to predict the coordination, although it could not resolve N_4, S_4, and S_2O_2 coordinations. Also, it was observed that spin- Hamiltonian parameter resolution was sufficient enough to distinguish between those vanadyl complexes present in porphyrins, humates, and minerals.

Molhatra and Buckmaster used 34 GHz ESR to determine the coordination around the vanadium ion in the three fractions separated by GPC from Boscan crude asphaltenes (39). Spin Hamiltonian parameters measured were observed to be consistent with those observed for $VO(N_4)$ coordination. This has suggested that vanadyl (V=O) was bonded to the porphyrin structure.

2.4.5- Gas Chromatography

The porphyrins and metalloporphyrins are too involatile to be analyzed

directly by a gas chromatography or by a combination of GC-MS. A study by Boylan and Calvin (48) showed that shielding of the macrocyclic nucleus with bulky trimethylsiloxy ligand attached to a central silicon ligand decreases intermolecular attractions, rendering it volatile that can be directly chromatographed at normal temperature and pressure. Boylan et al. (49) have, however, made modification in the synthetic procedure and produced excellent yields of bis(trimethylsiloxy) silicon derivative. Bis(trimethylsiloxy)silicon IV etioporphyrin I was synthesized and used as standard. The mass spectra of which showed a predominant ion at M^+ (m/e 682). It also showed an ion peak at M^+ - 89 resulting from a loss of a trimethylsiloxy ligand group.

Geoporphyrins separated from Boscan crude oil by acid demetallization technique and purified by the combination of TLC and adsorption chromatography were silylated and then analyzed by GC using two columns -glass beads coated with 0.1% Apizon L and with 0.1%SE-30. Electron capture and flame ionization detectors were used. Apizon coated column was claimed to give better separation. The GC eluents were collected by preparative techniques and analyzed by mass spectrometer. The retention times were observed to increase with increasing molecular weights. Both Etio and DPEP along with other homologs of porphyrins were observed when analyzed with mass spectrometer.

Eglinton et al. used computerized GC-MS for the analysis of petroporphyrins of Gilsonite bitumen and Boscan crude oil (50). The GC-MS

analysis of the bis(trialkylsiloxy)silicone(IV) derivatives of the petroporphyrins on capillary column coated with polar phase such as OV-1 or CPsil-5 resulted in the separation of various carbon number homologues of the DPEP, Etio, and other series present.

Marriott et al. reported the first capillary gas chromatographic method for the analysis of metalloporphyrins (51). The metalloporphyrins of Zn(II), Cu(II), Ni(II), V(IV), Co(II), Pd(II), Ti(IV), and Pt(II) were synthesized and analyzed by flexible fused silica capillary column. Using a short column, the above mentioned metalloporphyrins showed complete separation while that of the nickel and vanadyl octaethylporphyrin complexes showed incomplete separation.

Blum and Eglinton have recently come up with a new invention of high temperature stable glass capillary columns (52). These columns were coated with PS-090 (20% diphenyl substituted CH_3O- terminated polysiloxane). These columns were reported to provide a selective stationary phase for the direct analysis of metalloporphyrin complexes. These glass capillary columns were prepared from a medium polarity stationary phase bearing terminal methoxy instead of the reactive hydroxy. It was found to exhibit the highest temperature (= 430°C) stability among all commercially available polar and medium polar phases. This type of column when tested on model metallo porphyrin compounds has proved to be satisfactory for easier and quick GC analysis of such low volatile compounds.

Hein et al. (53) have developed an integrated analytical package for performing automated multicomponent analysis of GC/MS data by reverse search followed by additional data processing using a computer database. Improvement in reliability of interpretation and simplification of use were achieved. This package was meant for the analysis of geoporphyrins and to determine their distribution in a series of samples.

Hodgson et al. have employed the gas chromatography to study the range of alkyl substitution of the original porphyrins (54). The original porphyrins were separated by acid demetallation process, purified, and oxidized by chromic acid. The produced maleimides were analyzed by GC and GC-MS. Two major products of methyl ethyl maleimides with a smaller amount of what was believed to be monoethyl maleimides were detected upon oxidation of the gilsonite porphyrins. The maleimides which were produced upon oxidation were monomethyl, methyl ethyl along with what was thought to be methyl n-propyl. Oxidation of the Boscan crude oil porphyrins to maleimides gave five member maleimides series: monomethyl, monoethyl, methyl ethyl, methyl n-propyl, and ethyl n-propyl.

Barwise and Whitehead have used the gas chromatography to study the porphyrins from Boscan crude oil (55,56). The distillate was oxidized with chromic acid to maleimides and analyzed by capillary gas chromatography (GC) and GC/MS, it showed series of maleimides with side chains of C_1 to C_8. Two other peaks were identified as phthalimides which gave the first firm indication of the structure of the rhodo porphyrins.

2.4.6- Mass Spectrometry:

The major problem in determining the composition of porphyrins is that they are too involatile to be analyzed by gas chromatography (GC) or by a combination of gas chromatography and mass spectroscopy (GC/MS) using conventional columns. This problem has been overcome by the use of the direct inlet solid probe facility in the mass spectrometer instrument. This solid probe acts as a microdistillation device.

Hood and his coworkers published the first report of the mass spectra of nickel etioporphyrin-III and vanadyl etioporphyrin-I in 1960 (57).

In 1963 Dean and Whitehead reported a range of molecular weight of metalloporphyrins separated from high boiling distillate and residue (58). The mass spectra showed the evidence for the presence of homologous series of metalloporphyrins from C_{28} to C_{32}.

Thomas and Blumer reported the high voltage (70 eV) mass spectra of the separated porphyrins and their vanadium complexes from Triassic oil shale of Serpiano, Switzerland (59). Pigments having a range of C_{27} to C_{34} were found.

Morandi and Jensen (60) used the high and low voltage MS to analyze the porphyrins separated by acid extraction from oil shale, shale oil and petroleum from Mahogany Ledge of the Green River, Colorado, Green River shale and from Wilmingten, California. Two homologous series of porphyrins

with 7 to 13 methylene substituents per molecule were observed in oil shale and petroleum. Their visible spectra were of phyllo type. The MS of the porphyrins from the shale oil showed a complex mixture of Etio type. They also reported that low voltage MS produces mainly molecular peaks .

Baker reported the low voltage mass spectra of the acid extracted porphyrins for a number of asphaltenes (61). About a dozen homologs of deoxophyllo and Etio series were found to be present in a Gaussian-like distribution. The UV/Vis analysis of the chromatographically separated porphyrins confirmed the presence of Etio, phyllo, and small amounts of rhodo.

Baker et al. (62) analyzed the acid extracted petroporphyrins from asphaltenes from Agha Jari, Baxterville, Belridge, Boscan, Burgan, Mara Melones, Rozel Point, Santiago and Wilmington petroleums, as well as from gilsonite, Athabasca tar sand, and Colorado oil shale by low voltage (12 eV) mass spectrometry. They recommended a probe temperature of 260°C as suitable for obtaining mass spectra of porphyrin mixtures. Two homologous series of DPEP and Etio corresponding to molecular weight of 308 + 14n and 310 + 14n, respectively, where n is an integer of 2 or greater, were reported to be present. Also MS of rhodo porphyrins separated from Melones petroporphyrin mixtures was recorded and found to correspond to 456 + 14n and 458 + 14n. Based on these data, a structure of the rhodo porphyrin were proposed.

Yen et al. studied the mass spectra of petroporphyrins separated from Boscan, Mara, North Belridge and Agha Jari asphaltenes (63). Two major series: DPEP and Etio were found in addition to monobenzo etio and monobenzo DPEP porphyrins. Also, they detected a loss of phenyl or a tolyl group corresponding to M - 71 and M - 91 when the rhodo porphyrins were measured by high voltage spectrometer.

Didyk et al. (64) indicated that the petroporphyrins from the Cretaceous crude oil, La Paz, Venezuela was a mixture of Etio and DPEP homologues ($C_{30} - C_{39}$). The mass spectra of the oxidatively degraded petroporphyrins with chromic acid showed that a series of five maleimides were present: monomethyl, monoethyl, methyl ethyl, methyl n-propyl, and ethyl n-propyl. Rhodoporphyrin was also confirmed to be present from the UV/Vis data.

Quirke et al. (65) were able to isolate chromatographically eight predominantly single carbon number porphyrin fractions from a bitumen and gilsonite from Uinta basin, Utah. The mass spectrometry, UV/Vis absorption and ^1H NMR measurements showed that seven of these fractions were etioporphyrins ranging from $C_{29} - C_{32}$ and contained only methyl, ethyl and hydrogen substituents, with no meso alkyl groups. C_{31} and C_{32} DPEP were also confirmed to be present. Liquid chromatography, however, showed that C_{32} DPEP gave two peaks indicating the presence of two isomers of the same molecular weight as observed by MS.

Vaughan et al., (66) in response to the knowledge of the presence of high

molecular weight porphyrins in petroleum asphaltenes, reported the mass spectra, UV/Vis, infrared, ^1H NMR, and E.S.R analysis of ten synthetic meso tetraaryl porphyrins and thier vanadyl chelates. Mass spectra measured at high voltage showed fragmentation due to the loss of successive groups (66).

Barwise and Whitehead (55,56) used the low voltage (11 eV) mass spectrometer for the analysis of the vanadyl porphyrins separated from Boscan crude oil distillate (500 - 650 °C). The vanadyl porphyrins separated through silica gel and sulfonic acid functionalized silica gel column were shown to consist of C_{25} to > C_{50} of DPEP, Etio, Di-DPEP, Rhodo DPEP and rhodo etio type of porphtrins. The trapped fractions from HPLC were also analyzed by mass spectrometry. Rhodo porphyrins were reported to exist as assayed by its visible absorption peak at 590 nm. The mass spectra of which has indicated that the maximum peak was for rhodo etio at C_{32}.

Saoiabi et al. studied the vanadyl- and nickel porphyrins separated from the oil shale of Timahdit, Morocco (67). Mass spectra (measured at 30 - 70 eV), and visible bands ratio of α/β showed that there were only $C_{29} - C_{32}$ DPEP series of vanadyl porphyrins while there were $C_{28} - C_{32}$ of both Etio and DPEP series of nickel porphyrins.

Shaw et al. (68) reported CH_4 chemical ionization mass spectra (C.I. MS) of three standard porphyrins: two Etio (Etio-I and Etio-II) of C_{32} and octaethyl etio porphyrins, and petroporphyrin mixtures separated as nickel porphyrins from bitumen gilsonite of Uinta and then demetallated. The C.I.

MS analysis of these samples were also compared to their analysis by electron impact mass spectra (E.I. MS). Fragments $(M - 15)^+$ were observed in case of E.I. MS. The isotopic peaks of these fragments coincided with homologue molecular ions. However, the fragmentations were much reduced in case of C.I. MS resulting in an easier qualitative and quantitative analysis of complex mixture of petroporphyrins . A slight loss in sensitivity was reported to occur in C.I. MS as compared with E.I MS or field desorption (F.D.) mass spectrometry.

Bakirova et al. studied the vanadyl porphyrins from petroleum of different regions in Kazakhstan, U.S.S.R. (69). The mass spectrometry measurements indicated that the vanadyl porphyrins from Zhanatalan horizon was composed of Etio and DPEP, M and M-2 series. The M series ranged between 487 and 625 and M-2 series ranged between 527 and 653. The ratio of M to M-2 was reported to be slightly greater than one, which provided evidence of almost identical contents of porphyrin of homologous series (M and M-2). The visible absorption peaks ratio of α/β indicated that the absorption of Etio type was double that of the DPEP type. The porphyrins from Zhanazhol petroleum was reported to contain a wider range of homologous series (M, M-2, M-4, and M-6 series).

Burkova et al. used mass spectrometer to study the vanadyl porphyrins compositions from several Surgut petroleum fractions of West ern Siberia (70). All petroleums studied were found to contain Etio and DPEP types. The ratio of M-2/M was used to see the effect of the thermal oxidation and

bacteriological actions on the type and distribution of porphyrins. The resistance of the DPEP was found to be less toward the thermal oxidation and bacteriol action than the Etio type. The high molecular part of the homologous series was reported to decompose as well.

Ekstrom et al. (21) studied chromatographically separated porphyrins from Julia Creek deposit using insertion probe, fast atom bombardment (FAB) and field desorption (FD) mass spectrometry techniques in addition to electronic absorption technique. The mass spectra obtained using EI and hydrogen CI ionization were found to be similar except that the peaks in the CI spectra were located one mass unit higher than the corresponding EI peaks. The FAB spectra of one sample was found to be different than the corresponding EI mass spectra. The FAB showed not only a different distribution of peaks in the range of 500-600 atomic mass unit (amu) but also yielded a second set of prominent peaks in the range of 1022-1078 which corresponded to (M-4) ± 14n.

Xieqing et al. reported the high voltage mass spectra of the porphyrins from Liaohe-Gaosheng oil, China (71). The porphyrins were separated as nickel porphyrins by means of adsorption chromatography and then demetallated by methane sulfonic acid. The mass spectra of the demetallated porphyrin complex showed the presence of homologous series of Etio, DPEP, Di-DPEP, Rhodo-Etio, Rhodo DPEP, and Rhodo DPEP. Centrifugal thin-layer chromatography (CTLC) was used to further separate the porphyrin mixtures into eight fractions of different R_f. Mass spectra of each fraction was

observed to be different from each other. Rhodo porphyrin was reported to have higher R_f value from those of non rhodo type. CTLC was shown to be more effective in isolation of porphyrin mixtures and could speed up the separation procedure by a factor of 2-3 while keeping the same R_f as conventional TLC.

Jhonson et al. employed tandem mass spectrometry (MS/MS) for the characterization of high-carbon number > C_{33} geoporphyrins (72). MS/MS allowed selection of molecular ions of individual carbon number porphyrins of the DPEP and Etio types for fragmentation by collisionally activated dissociation. Structural information of those porphyrins can be achieved by comparison of their daughter and neutral loss spectra with those of porphyrin standards. Mass spectra of the metallated and demetallated porphyrins were reported to be the same which suggested less sample pretreatment requirements for analysis. Also, MS/MS was found to be well suited for analysis of such complex mixture of porphyrins as compared to the electron ionization mass spectrometry.

Sundraraman et al. reported the first application of the combinatio n of H_2 C.I. and MS/MS to porphyrins and metalloporphyrins (73). High voltage (70 eV) and direct insertion probe were used for the analysis. Copper Etio-I, nickel Etio I, and vanadyl Etio- II were observed to give fragmentation leading to ions of mono-, di- and tripyrrolic ions. The daughter ion spectra of M^+, $(M+2H)^+$, $(M+4H)^+$, and $(M+6H)^+$ ions by MS/MS technique showed fragmentation by cleavage of substituent groups attached to the pyrrole rings.

Therefore, it was stated that the combination of these two techniques provides information on the nature of the substituents attached to the pyrrolic rings.

Blumer and Rudrum used mass spectrometer along with UV/Vis spectrophotometer and infrared to study the high molecular weight fossil porphyrins (33). These porphyrins were separated from a Triassic and a Pennsylvanian oil shale by means of gel permeation chromatography and adsorption chromatography. The mass spectra, UV/Vis spectra, and the IR spectra indicated that the less polar group pigments consisted of several homologous series of tetrapyrrole ring monomers with long chain alkyl substitution. The more polar pigments were homologous porphyrin dimers. The mass spectra were recorded using programable heated probe from 150°C to above the pyrolysis temperature because the fractional distillation of porphyrins which differed in their volatility gave more structural information. It was observed that highly alkyl substituted porphyrins pyrolyzed well below 260°C, which suggested that the initial pyrolysis temperature was structure dependant.

Shilonosova et al. (23) employed the mass spectrometer to analyze the fractions separated with HPLC and to identify certain vanadyl porphyrin compounds of crude oil and vacuum gas oil from West ern Siberia. It was found that each HPLC peak corresponded to a porphyrin with a specific molecular mass. However some of the vanadyl porphyrin homologs present in crude oil and gas oil were reported to be in two isomeric forms differing in retention time in the column. It was concluded that distillation of the crude

oil resulted in partial differentiation of the composition of the vanadyl porphyrins contents of crude oil and gas oil.

Mozzhelina et al. reported the MS analysis of the vanadyl porphyrins from West ern Siberia and Sakhaline petroleums (19). Homologues corresponding to two series, Etio and DPEP, were found to exist in all oils examined. The intensities of the molecular peaks of these series were also recorded. Thin layer chromatography showed elongated spots. The HPLC chromatograms, however, confirmed the heterogeneity of the vanadyl porphyrins.

In another study Mozzhelina et al. (22) analyzed the vanadyl porphyrins from Sakhaline oils and Ekhabi taken at different depth with mass spectrometer. The mass spectra showed that all the oils had similar vanadyl-porphyrins structural-group composition.

Sebor employed high voltage mass spectrometer to analyze the vanadyl- and nickel porphyrins of a rock extract from the Gulf area (34). The vanadyl- and nickel porphyrins were separated by means of adsorption chromatography and gel permeation chromatography successively. The trapped fractions were analyzed by mass spectrometer and showed different homologous series of Etio and DPEP of both vanadyl and nickel porphyrins.

Shul'Ga et al. have determined the homologous series of the vanadyl porphyrins from West Surgut deposit, U.S.S.R. (20). Mass spectrometric data showed that the vanadyl porphyrins consisted of DPEP with its $C_{30} - C_{31}$

homologues and an Etio with a C_{10} lateral alkyl branch in the porphyrin ring.

Serebrenmkova et al. (74) employed the low resolution mass spectrometer to elucidate the differences in R_f of the vanadyl porphyrins separated from Sovetskoya and Kokayty deposits. They showed that the vanadyl porphyrins were of DPEP and Etio types. The intensity of each molecular peak of each series was reported alongwith the M/M-2 ratios. The length of the side alkyl chains were deduced by metastable-ion mass spectrometry. The maximum length of the alkyl chain varied from 2 to 8. The vanadyl porphyrins from various sources with identical R_f had the same fragmentation patterns.

Hodgson et al. (54) analyzed the demetallated porphyrins from gilsonite, Boscan crude, Venezuela and the Lloydminster, Canada, by mass spectrometry. The oxidation of porphyrins to maleimides was studied by GC-MS. The MS data showed that gilsonite sample exhibited a symmetrical etioporphyrins with a major homolog at 464 amu. A similar etioporphyrin series was found in Lloydminster crude with the largest homolog appeared at 478 amu. Boscan crude showed both Etio and DPEP with eleven homologs for DPEP and seven for Etio.

2.2.4.7- Crystallographic Methods:

The crystallographic method is less frequently used due to the major difficulty of growing crystals of sufficient quality when working with small amounts (< 1mg) of sample. The technique is however used to characterize and determine the structure of porphyrins and metalloporphyrins.

Fleisher has determined the crystal structure of the nickel etioporphyrin I (75). The calculated bond length and angles of the molecule showed that the molecule was non-planar, being distorted by having two of the pyrrole ring bent up and two bent down from the plane formed by the four-corner methene carbon atom.

Ekstrom et al. (76) reported the structure of a vanadyl porphyrin compound isolated from oil shale from the Julia Creek deposit, Australia, by X-ray crystallography. The vanadyl porphyrin was obtained by chromatographing the chloroform extract of the deposit on Merck Kieselgel-60. The vanadyl porphyrin band was separated further by HPLC (C18 column) into seven peaks. The predominant peak was selected and isolated on a semipreparative column and MS analysis of which showed two molecular peaks at 527 and 541 amu. Preparative TLC (silica gel) of this gave two bands. The less polar (541 amu) was obtained as a single crystal. The structure was determined to be C_{32} DPEP.

CHAPTER 3

EXPERMINTAL

3.1- Distillation of the Crude Oil

3.1.1- True Boiling Point Distillation:

The true boiling point (TBP) distillation of the Arabian Heavy crude oil was carried out in an all-glass semical 298 (Podbielniak Inc. Ill., U.S.A.) distillation apparatus. The apparatus consisted of a column (3.3 feet x 1.0 in) which was packed with heli - pack 2917, (0.05 x 0.10 x 0.10) inch packing material made of nichrome. The column had an efficiency of 15 theoretical plates and was connected from the bottom to a three - neck distillation kettle of a volume of 5 liter. It was also connected to two distillate receivers (200 ml each), cold water was used for the condenser as well as for cooling the main body of the column. The kettle was provided with a thermometer and a nitrogen purge supply. Heating mantles were used to provide heating requirement for the distillation process. A vacuum pump was also provided for conducting distillation at reduced pressure.

A homogeneous sample of 4.0 liter of Arabian Heavy crude oil was transferred to the distillation kettle. The kettle was connected to the column and covered from the top and the bottom with heating mantles to provide a uniform heating supply for the sample to be distilled. The receiving flasks were also connected to the column and checked for leaks before heating was

started. The distillation was initially carried out at the atmospheric pressure and continued at a kettle maximum temperature of 280°C and a vapor temperature of 200°C. The reflux ratio was maintained at 5:1 throughout the distillation.

To avoid an expected cracking of the crude oil's components at higher temperature, the distillation was conducted at a reduced pressure. All connections were greased and checked for leaks before the distillation was resumed. A pressure of 30-40 mm Hg and a reflux ratio of 5:1 were maintained throughout the process. Slow stream of pure nitrogen was kept bubbling through the contents of the distillation kettle to facilitate the boiling and to remove trace of any oxygen present. The reduced-pressure distillation was continued until the kettle reached a temperature of 280°C and that of the vapor reached 220°C.

3.1.2- Wiped-Film Molecular Still Distillation:

At temperature higher than 300°C severe cracking of the components of the crude oil takes place. For this reason the high boiling fractions from the crude oil were obtained by passing the residue obtained from TBP distillation through a Wiped-Film Molecular still.

The apparatus consisted of a feed-degasser flask located at the top and connected to the main body of the still, evaporator, by means of a narrow tube containing a valve that allowed the feed to run down to the evaporator. The evaporator was equipped with three sets of teflon wipers which were

placed vertically and around the evaporator. These wipers were rotated at a constant speed by a rotating motor placed on top of the apparatus. The apparatus was also equipped with a high efficiency pumping system consisting of a rotary pump and a diffusion pump. Heating mantles were also used to supply heat. A thermocouple was inserted between the heating mantle and the outside wall of the still to register the temperature.

All joints were vacuum sealed and checked for leaks. The teflon valve mentioned above was closed and the residue that was obtained from the TBP was charged to the feed flask. The main body of the still and the feed flask were covered with a heating mantle to provide uniform and constant heat for the vacuum distillation process.

The system pressure was maintained at 0.1 mm Hg. When the desired temperature of the system reached 264°C (equivelant to 535°C at atmospheric pressure), the rotating motor was turned on to rotate the wipers and the feed was slowly introduced to the evaporator part of the still through the valve, mentioned above, to avoid fluctuation in both of the pressure and the temperature accordingly. As the wipers rotated, they spread the feed on the walls of the evaporator into a thin film as it reached. The volatile components of the feed condensed on the water-cooled inner surface which was concentric to the heated evaporator. The condensed distillate ($< 535°C$) flowed down the cold surface and collected in the receiver connected at the bottom. The residue ($> 535°C$) that remained on the heated walls flowed to the other receiving flask connected at the bottom. The process continued in this

manner until the feed was finished. The process was repeated once again under the same conditions above using the residue (> 535°C) collected above as a feed to ensure complete removal of the distillate (225 - 535°C).

3.1.3- Boiling Range Distribution of the Distillate and Residue:

The distillate and the residue obtained above were subjected to simulated distillation by means of a gas-liquid chromatography according to ASTM D 2887 - 76 method using a Hewlett-Packard 5880 gas chromatograph.

The sample was dissolved in toluene, and 0.3 microliter of this solution was introduced into the gas chromatograph. The initial temperature of the column was set to 35°C and heated up to the final temperature of 350°C. at a programmed rate of 10°C/min. The final temperature was held for 10 minutes. The gas chromatography-separated hydrocarbons of the sample were in the order of their boiling points.

A calibration curve was made under similar condition using standard hydrocarbon mixture covering the same boiling range as was expected to be covered by the hydrocarbons present in the sample. The boiling temperature recorded were assigned to the time axis and the instrument response to the other axis. The area under the curve formed was recorded throughout the run. The initial boiling point was assigned to the first 0.5 % of the total area, whereas the final boiling point of the sample was assigned to the 99.5% of the total area.

3.2- Asphaltenes Separation From Arabian Heavy Crude Oil & Residue:

Asphaltenes from the Arabian Heavy crude oil and residue were precipitated by the addition of 20 volumes of n-heptane to the crude oil. The mixture was stirred, allowed to stand for 16 hours, and then centrifuged at 3500 rpm for 60 minutes. The supernatant liquid was decanted and fresh n-heptane was added to the residue, the mixture was stirred and centrifuged again. The asphaltenes were collected from the bottom of the centrifuging tube, washed with n-heptane, dried in a vacuum oven at 60°C and weighed as impure asphaltenes. These asphaltenes were purified by Soxhlet extraction with n-heptane for 24 hours and then dried in a vacuum oven at 60°C. The dried asphaltenes were weighed.

The elemental analysis of the carbon, hydrogen, nitrogen, and sulfur were done on a Carlo Erba elemental analyzer model 1106.

3.3- Separation of Nickel and Vanadyl porphyrins from Residue:

3.3.1- Method No. 1:

The method developed by Barwise and Whitehead was followed (56). A glass column (60 x 2.54 cm) was dry packed with 150 grams of silica gel (Ficher Scientific Company, New Jersey, U.S.A.; 80 - 200 mesh) that was activated at 250°C for 24 hours. A sample of the residue (2.5 grams) was transferred to the column and eluted with solvents of increasing polarity. The saturates were eluted with n-heptane. Then the aromatics were eluted with

toluene. Finally, the resins were eluted with ethylacetate. The solvents were evaporated by means of a rotary evaporator under vacuum and finally dried under nitrogen stream. Each fraction was monitored by ultraviolet/visible absorption (UV/Vis) spectrophotometer for the presence of metalloporphyrins absorptions and X-ray fluorescence (XRF) for the determination of the concentration of vanadium and nickel.

3.3.2- Method No. 2:

The method developed by Barwise and Whitehead (56) was modified. A glass column of the same size as above was dry-packed with 150 grams of previously activated silica gel (80 - 200 mesh) at 250 °C for 24 hours. The residue sample (2.9 grams) was transferred to the top of the column and eluted with successive solvents of increasing polarity. Saturates were eluted with normal heptane. Then the sample was eluted with 1:1, 1:2, and 1:3 (v/v) of toluene/n-heptane. Next it was eluted with pure toluene followed by ethyl acetate respectively. All fractions were freed from solvents by the rotary evaporator and then dried under nitrogen stream. The dry fractions were analyzed by UV/Vis spectrophotometer and XRF.

The eluates obtained above were mixed and rechromatographed on similar type of column as above. The sample was eluted with toluene followed by ethylacetate. Solvents were evaporated from the fractions by using the rotary evaporator and then finally dried with nitrogen stream. These fractions were all analyzed by spectrophotometer and XRF.

The toluene eluate was charged to a thin layer preparative silica gel plate (Whatman Inc. U.S.A.) by means of a capillary tube. The solvent was allowed to dry and the plate was developed in a glass box containing 1:1 cyclohexane/methylene chloride. The bands observed were scratched and extracted in methylene chloride and analyzed by UV/Vis spectrophotometer.

3.3.3- Method No. 3:

The separation method developed by Spencer et al. was followed (27). This method involves the separation of the residue and its asphaltenes into two groups: porphyrins and nonporphyrins. The residue sample (3.4 g) was dissolved in minimum toluene and adsorbed in neutral alumina (BIO-RAD Laboratories, Calif., U.S.A.; 50 g) and charged to a glass column (80 cm x 2.54 cm) already packed with fresh neutral alumina (100 g). The porphyrinic fraction was eluted by dimethylformamide (DMF). The column was then washed with chloroform to elute the "nonporphyrins". The DMF eluate was extracted in a separatory funnel in chloroform (5 x 20 ml). The DMF was washed by water (5 x 100 ml). The chloroform-containing porphyrins were preadsorbed on a silica gel (80-200 mesh) and dry-packed in a glass column (50 x 1 cm). The column was eluted by successive solvents of increasing polarity: 1:9, 3:7, 1:1 chloroform/n-hexane and chloroform respectively. The fractions were freed from the solvents by rotary evaporation and then dried under nitrogen stream. The fractions were then analyzed by UV/Vis spectrophotometer (350-650 nm). The vanadium and nickel concentrations

were measured by XRF.

The first three fractions above were analyzed by thin layer chromatography on analytical silica gel plates. A sample of each was charged to the plate, which was previously activated at 120°C for half an hour, by means of a capillary tube and developed in 1:1 methylene chloride/cyclohexane.

3.3.4- Method No. 4:

The method described as Method No. 3 was applied on the asphaltenes precipitated from residue for the separation of vanadyl or nickel porphyrins.

3.3.5- Method No. 5:

HajIbrahim's (9) method of liquid extraction of metallopetroporphyrins along with the method developed by Chakraborty and Bhatia (42) were used after some modifications. A residue sample (6 grams) was dissolved in minimum toluene and 10 grams of cellulose powder were added to break the emulsion. Methanol (100 ml) was added and the mixture was sonnicated for 15 min. The extracts were centrifuged at 3500 rpm and filtered, and then adsorbed on silica gel(100- 200 mesh, 80 g). The solvent was rotary evaporated at reduced pressure from the silica gel sample mixture. The mixture was packed in a glass column (80 x 2.54 cm) that was already packed with dry silica gel (100 g). Then it was eluted initially with cyclohexane, and next it was eluted with increasing polarity of benzene in cyclohexane (1:4 and 3:7) followed by pure benzene and 1:1 benzene/ethylacetate and, finally, with

pure methanol. The solvents were rotary evaporated. Each fraction was monitored by UV/Vis spectrophotometer for the presence of vanadyl and/or nickel porphyrins. Also the above fractions were analyzed by XRF for vanadium and nickel contents.

The fractions previously eluted with benzene, ethylacetate/benzene (1:1), and methanol were mixed up together and adsorbed on alumina (Fisher Scientific Company, New Jersey, U.S.A.; 80-200 mesh; 70 grams) and packed on the top of dry alumina (100 grams) in a glass column (80 cm x 2.54 cm). This was eluted with benzene/cyclohexane (1:19), methylene chloride/n-hexane (1:1), and, finally, with methylene chloride. The solvents were rotary evaporated. The fractions were monitored by UV/Vis spectrophotometer for the presence of vanadyl porphyrins. The concentrations of vanadium and nickel were measured by XRF.

3.3.6- Method 6:

Separation of Nickel and Vanadyl Porphyrins from Arabian Heavy Asphaltenes:

3.3.6.1- Asphaltenes Extraction:

The method developed by Chakraborty and Bhatia (42) was used after some modifications. A 10.0 gram sample of the asphaltenes obtained directly from crude oil by precipitation were extracted in a Soxhlet extractor with 3:17, 6:17, 12:17, 1:1, and 2:1 benzene/acetonitrile (v/v) each at a time. Every extracted portion of the above were freed from the solvent by a rotary

evaporator, dried under nitrogen stream, and weighed.

The above extractions were monitored by UV/Vis spectrophotometer for the presence of vanadyl and/or nickel porphyrins absorption peaks.

3.3.6.2- Separation of Vanadyl and Nickel Porphyrins from Asphaltenes Extracts:

The asphaltenes extracts obtained above were mixed after they were dissolved in a minimum amount of methylene chloride. The mixture was adsorbed on 80 grams of silica gel (Davison Chemical, Maryland, U.S.A.; 100-200 mesh). The silica gel- sample mixture was dried by means of a rotary evaporator and packed on top of 100 grams of of dry silica gel in a glass column (80 cm X 2.54 cm). The column was eluted with solvents of increasing polarity: cyclohexane, benzene:cyclohexane(1:4, 3:7, and 1:1), benzene, benzene:ethylacetate (1:1), ethylacetate, and methanol. Solvents were rotary evaporated. The eluates were monitored by UV/Vis spectrophotometer.

The last three eluates were dissolved in a minimum amount of methylene chloride and then mixed up together and adsorbed on alumina (Fisher Scientific Company, New Jersey, U.S.A.; 80-200 mesh; 80g). The alumina sample mixture was dried by rotary evaporation and packed on top of dry alumina (100 g) in a glass column (80 cm x 2.54 cm) and eluted with benzene/cyclohexane (1:19), methylene chloride/n-hexane (7:3 and 1:1), and methylene chloride.

In order to separate nickel porphyrins from the vanadyl porphyrins the benzene/cyclohexane(1:4, 3:7, and 1:1), and benzene eluates were mixed together and adsorbed on silica gel (Davison Chemical, Maryland, U.S.A.; 100-200 mesh; 60g) and packed on top of already packed 80 grams of dry silica gel in a glass column (100 cm x 1.5 cm). This was then eluted successively with benzene/cyclohexane (1:49), methylene chloride/n-hexane (1:9, 1:4, 3:7, and 1:1), methylene chloride, and methanol.

For thin layer chromatography, multi channel silica gel analytical plate was used. The plate was activated at 110°C for half an hour in an oven. The sample of vanadyl porphyrins (obtained from 3:7 methylene chloride/n-hexane eluate from the alumina column above) was dissolved in a minimum amount of methylene chloride and charged to the plate by means of a capillary tube. The plate was allowed to dry and then developed in a jar containing 1:1 decane/chloroform until the solvent front is 3 cm from the top end of the plate. The three bands observed were scraped and extracted in methylene chloride and analyzed by the UV/Vis spectrophotometer.

3.4- Instrumental Analysis:

3.4.1- Ultraviolet/Visible Spectrophotometric Analysis:

The ultraviolet/visible spectrophotometric (UV/Vis) analysis were performed on a double beam spectrophotometer, Cary (Varian, model 2390). A cuvet (1 cm in width) was used for measuring the UV/Vis absorptions of the

samples. The sample was dissolved in methylene chloride and transferred to the cuvet. Necessary dilution were made in methylene chloride. Methylene chloride was used as a blank in all the cases. The samples were scanned from 700 to 350 nm. The absorption data were reduced through the software facility attached to Cary.

3.4.2- X-Ray Fluorescence:

The vanadium and nickel contents of the samples were analyzed by x-ray fluorescence, XRF, (Kevex 700). The samples were dissolved in minimum toluene and transfered to containers. The containers were then charged to the XRF autosampler. The data were acquired and reduced by the computer software attached to the instrument.

3.4.3- High Performance Liquid Chromatography:

The high performance liquid chromatography (HPLC) instrument used in this study was Waters Associates, Milford, Mass., U.S.A.. The instrument is equipped with two pumps (Waters 501), programatic variable multiwavelength detector (Waters 490), and a data station (digital, proffessional 380). Solvent systems that were used were isocratic or gradient. The columns were 5μ (25 cm x .46 mm) C18 (Waters Assoc.). The samples were dissolved in minimum methylene chloride and loaded to the injection loop by means of a 10μl syringe needle. Two to three μl of sample was used for injection. Detection (UV/Vis) was conducted in all runs at 405 nm.

3.4.4- Mass Spectrometry:

The instrument used was Jeol (JMs-DX 300) provided with a data system (JMA-DA 5000). Direct probe were used to charge the sample into the heart of the mass spectrometer. The samples analyzed were dissolved in minimum methylene chloride and charged to glass cups, which were already probed and scanned under the same conditions, by means of a micro syringe. The solvent was allowed to evaporate and then the sample was inserted in the probe of the mass spectrometer. A programmed temperature from 70 to 350°C at 16°C/min was used. Low voltage of 18 eV and a current of 4 μA were used. The mass spectra were measured over a range of scans to account for the differential volatility of the porphyrin complexes.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1- General Characteristics of Arabian Heavy Crude Oil:

Arabian Heavy crude oil used in this study was obtained from Saudi Aramco. It comprises crude oil from an offshore field, Saffaniya, the world's largest petroleum field.

Besides Arabian heavy, Saudi Aramco produces three other marketable quality crude oils, namely: Arabian medium, Arabian light, and Arabian extra light. The four Arabian crude oils represent a wide range of crude oil types. Arabian heavy is the heaviest while Arabian extra light is the lightest among the four crude oils. The bulk properties of the four crude oils are tabulated in Table 1. Specific gravity, viscosity, carbon residue, ash content, sulfur, nitrogen and metals show a gradual increase from Arabian extra light to Arabian heavy crude oils. Nickel and vanadium compositions are generally low for the four crude oils. Since Arabian Heavy has the highest content of nickel and vanadium among the four Arabian crude oils, it was selected for the present study.

The 370 – 535°C distillate and 535°C+ residue, prepared by the TBP and the molecular distillation, were analyzed for their bulk properties, gravimetric yields and composition. The boiling range of the distillate was further confirmed by gas chromatography using ASTM D2887 method (77). Figure 1

Table 1- General Properties of Crude Oils

Test	Method(ASTM#)	AEXL	AL	AM	AH
Gravity °API	D 287	38.7	34.0	30.5	28.1
Ash, ppm	D 482	20	44	58	110
Pour Pt. °C	D 97	-17.8	-15.0	-12.2	-23.3
Sediment & water	D 96	Trace	Trace	Trace	Trace
Sulfur, % Wt	D 129	1.10	1.81	2.59	3.35
C Residue,% Wt.	D 189	2.0	3.58	5.87	7.53
Vanadium, ppm		3	15	28	69
Nickel, ppm		1	3	8	21
Nitrogen, % Wt.		0.04	0.10	0.12	0.16

AEXL = Arabian Extra Light, AL = Arabian Light, AM = Arabian Medium, AH = Arabian Havy

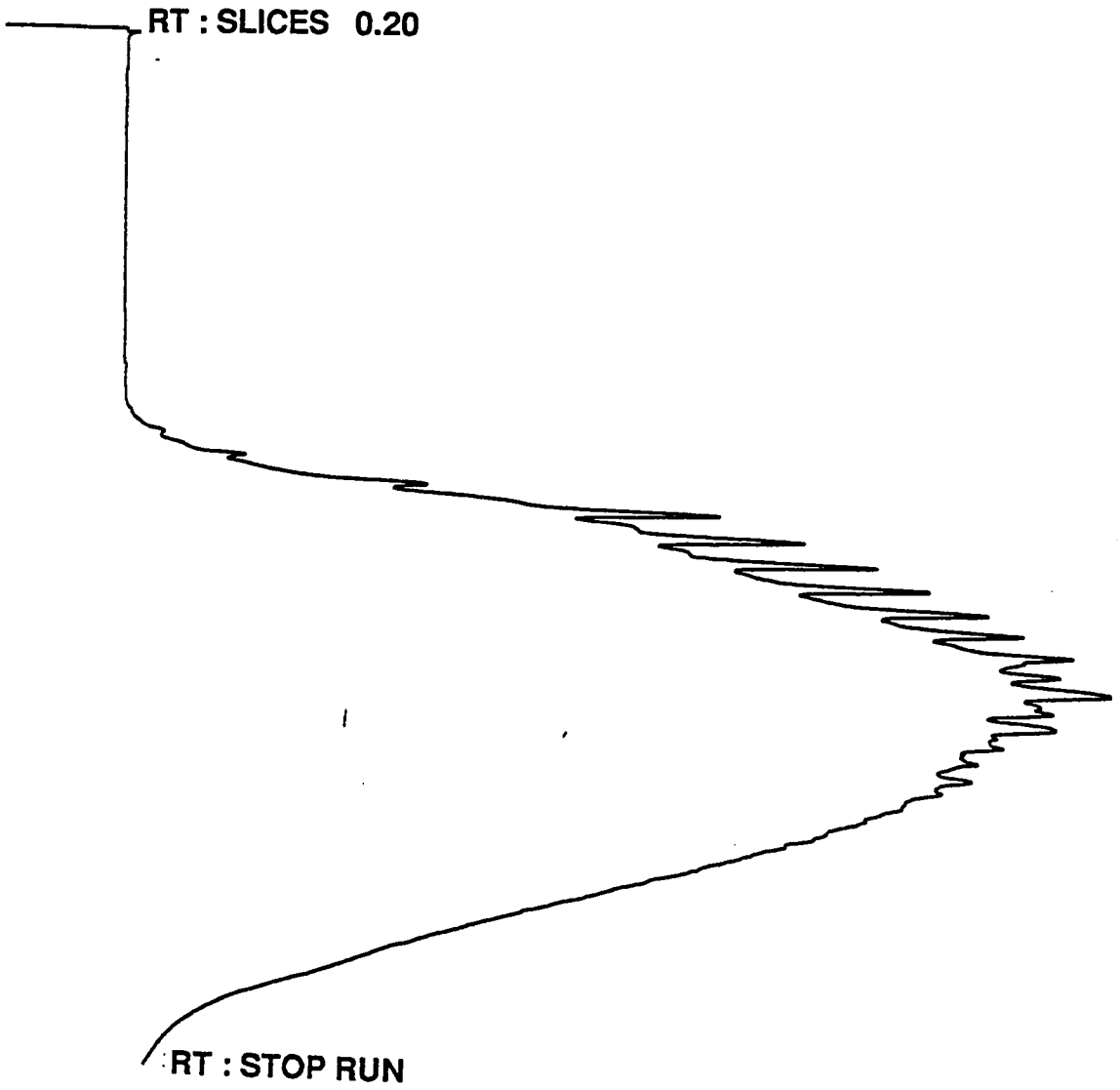


Figure (1) : Simulated distillation of Arab Heavy distillate by gas chromatography

shows the chromatogram obtained for the Arabian Heavy distillate. Boiling range distribution data indicated a very good agreement between the boiling points indicated by pressure-temperature relationship in the molecular distillation still and simulated distillation data. The physical and the chemical properties of the distillate and the residue along with crude oil are displayed in Table 2.

X-ray fluorescence analysis of the nickel and vanadium contents indicated that Arabian Heavy crude oil contained vanadium (69 ppm) and nickel (21 ppm), its distillate had a nondetectable amount of nickel and only 3 ppm of vanadium, and the residue cut contained 189 ppm of vanadium and 62 ppm of nickel. The asphaltenes contained 710 ppm of vanadium and 195 ppm of nickel. The residue cut and the asphaltenes contained about three times as much of vanadium contents as in the crude oil. The nickel contents of the residue and asphaltenes are 3 to 5 times more than that of the crude. On the basis of these results, the Arabian Heavy crude residue and asphaltenes were chosen for this study.

Premilinary UV/Vis spectrophotometric analysis of Arabian heavy crude oil and its residue showed no characteristic absorption peaks for nickel or vanadyl porphyrins (figure 2). This may be referred to the nature of the matrix of the sample that may cover the absorption of the metalloporphyrins. Therefore, it was thought necessary to separate metalloporphyrins from the residue and asphaltenes matrix before they were analyzed.

Table 2- Physical Prperties and Elemental Analysis

	Arab Heavy Crude	**Distillate**	**Residue**	**Asphaltenes**
Vanadium(ppm)	69	3	189	710
Nickel(ppm)	21	*	62	195
C (wt%)	83.3	85.2	85.3	81.9
H (wt%)	12.0	12.0	10.2	7.4
N (ppm)	1600	1000	4600	9500
S (wt%)	3.35	3.38	5.50	7.61
C Resid.(wt%)	7.53	12.36	13.91	-
API(60/60 °F)	26.7	18.6	3.2	-
Vis. (cs)	21.5@40 °C	29.5@100 °C	-	-
Pour Pt.(°C)	-10	18	70	-

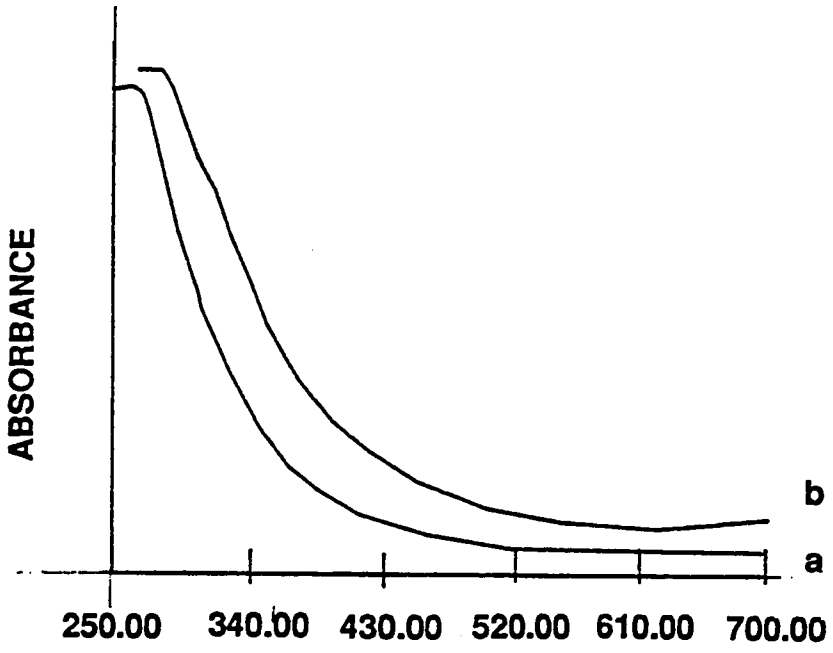


Figure (2) : UV-VIS spectrum of (a) Arab heavy crude (b) Arab heavy residue.

4.2- Chromatographic Separation of Nickel & Vanadyl Porphyrins from Residue Cut:

4.2.1- Method No. 1:

The chromatographic separation of vanadyl and nickel porphyrins from Arabian Heavy crude residue was performed according to the method developed by Barwise and Whitehead (56). The residue was fractionated by a silica gel column into three fractions: saturates, aromatics, and resins by eluting the column with three solvents of increasing polarity: n-heptane, toluene, and ethylacetate respectively. The saturates fraction was put away. The vanadium content of aromatic and resin fractions was determined to be 42 and 90 ppm respectively. While the nickel content was 32 and 3 ppm respectively. Nickel appeared to concentrate in the aromatic fraction. The vanadium was, however, found in both aromatic and resin fractions. The UV/Vis spectrophotometric analysis showed a weak absorption band at ca. 407 nm, characteristic for porphyrinic metal material in the eluates (figure 3).

The toluene eluate was further purified by using analytical thin layer silica gel plate developed in methylenechloride/cyclohexane (1:1). Three bands were observed: bottom, middle, and top. Only the middle band when scraped and extracted in methylene chloride was found to show UV/Vis absorption at 407 nm, characteristic of metalloporphyrins (figure 4).

The recovered middle band was again developed on the same type of TLC plate under similar conditions. Similar three bands were observed. Only the

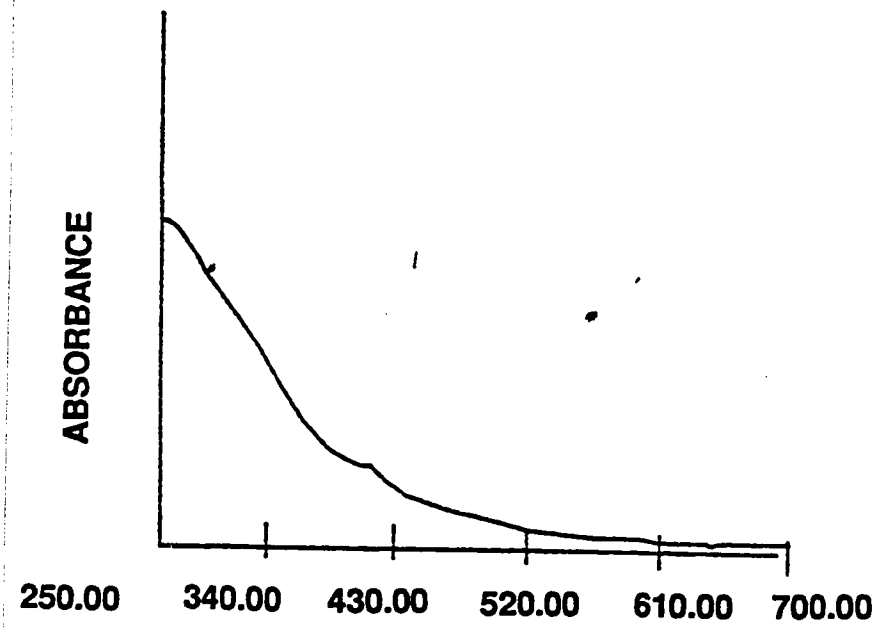


Figure (3) : UV-VIS spectrum of toluene eluate from Arab heavy residue.

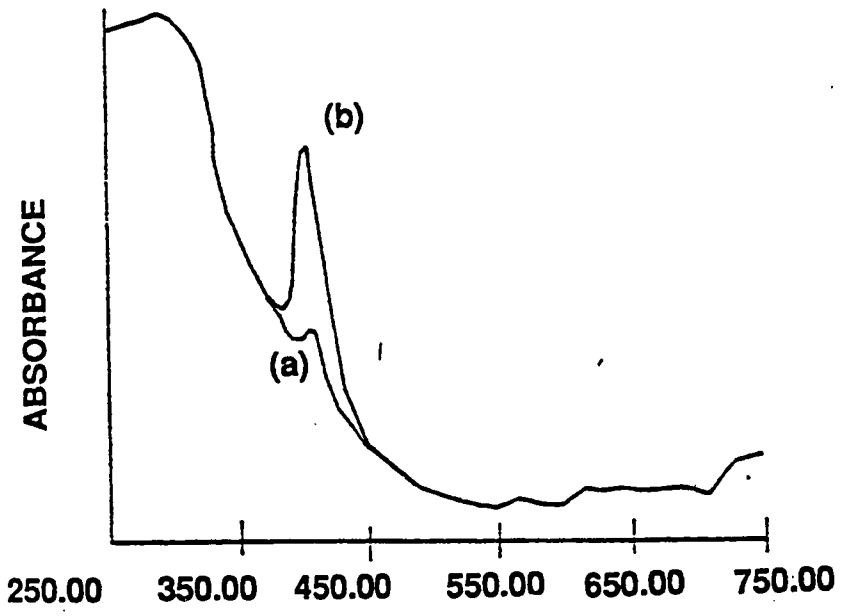


Figure (4) : UV-VIS spectra of toluene of (a) TLC middle band and (b) TLC middle band of (a)

middle band of which was observed to give absorption peaks at 409, 530, 570, and 590 nm (figure 4). These absorption bands are characteristic of vanadyl porphyrins. The top and the bottom bands showed no porphyrinic absorption.

4.2.2- Method No. 2

Since the above method did not produce good separation of nickel and vanadyl porphyrins based on the UV/Vis spectrophotometry and XRF data, the method was slightly modified. The residue sample was charged to the top of the dry-packed activated silica gel column and eluted successively with n-heptane, toluene/n-heptane (1:1, 1:2, and 1:3 v/v), pure toluene and ethylacetate. None of these eluates, however, showed UV/Vis absorption characteristic of metalloporphyrins. This may be referred to either the very low concentration of the porphyrin aggregate in each fraction or to the presence of contaminants that masked the porphyrin UV/Vis absorptions. Therefore, these eluates were mixed and charged to a second silica gel column where they were eluted successively with toluene and ethylacetate. Only the toluene fraction showed a weak absorption peak at 407nm, characteristic of metalloporphyrins (figure 5).

4.2.3- Method No. 3:

Since the above two methods did not give satisfactory separations, another method was tried.

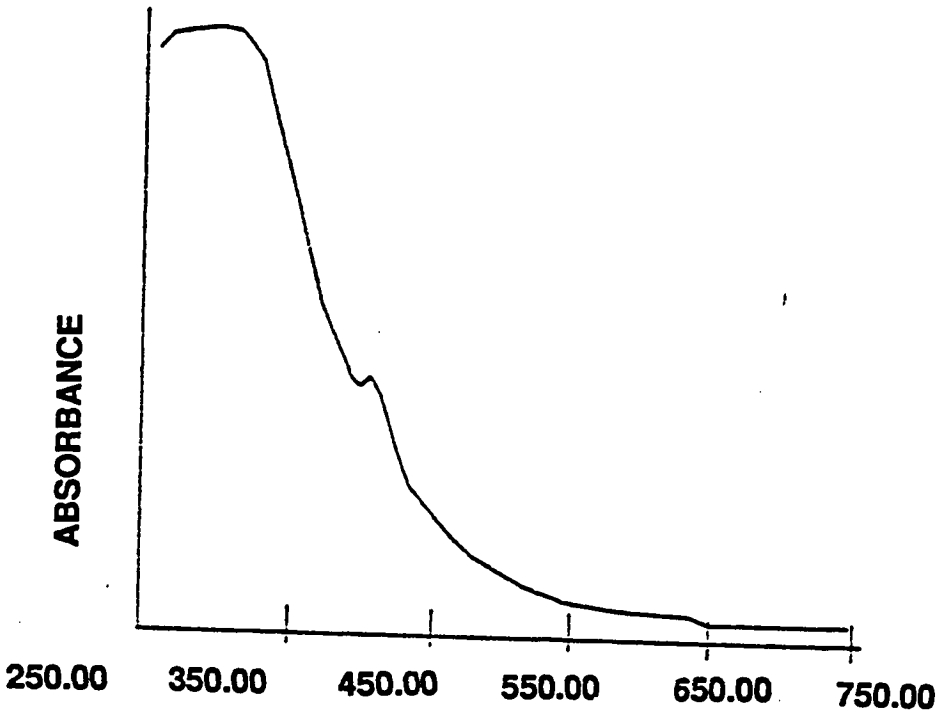


Figure (5) : UV-VIS spectrum of toluene fraction from Arab heavy residue.

The method described by Spencer et al. (27) was used. A sample (3.4 g) of the residue was charged to a column packed with neutral alumina and eluted with dimethylformamide (DMF).

This DMF eluate was extracted with chloroform and adsorbed on a silica gel and packed in a glass column containing 80 grams of silica gel. This was eluted with different proportions of chloroform in n-hexane (1:9, 3:7, 1:1) and finally with chloroform. The 1:9 chloroform/n-hexane eluate (7.1 wt% of the residue sample) gave no characteristic UV/Vis absorption for nickel porphyrins as it was claimed by Spencer et al.(27) nor any UV/Vis absorption characteristic of any other metalloporphyrins. The fraction eluted with 3:7 chloroform/n-hexane (5 wt% of the residue sample) had UV/Vis spectrophotometric absorption at 570 and 530 nm, characteristic absorption of vanadyl porphyrins (figure 6). The 1:1 methylene chloride/n-hexane eluate (4 wt% of the residue sample) gave UV/Vis absorption bands characteristic of vanadyl porphyrins (figure 7), and contained 266 ppm vanadium and 19 ppm nickel as detected by XRF.

The TLC purification of 1:1 methylene chloride/n-hexane gave enhancement of the UV/Vis absorption peaks (figure 7). The fraction eluted by methylene chloride showed no UV/Vis absorption characteristic of metalloporphyrins and also no nickel nor vanadium was detected by XRF. Although XRF analysis of 1:1 methylene chloride/n-hexane showed the presence of nickel, there was no indication for nickel porphyrins in the eluate as measured by UV/Vis spectrophotometry. This was thought to be due to

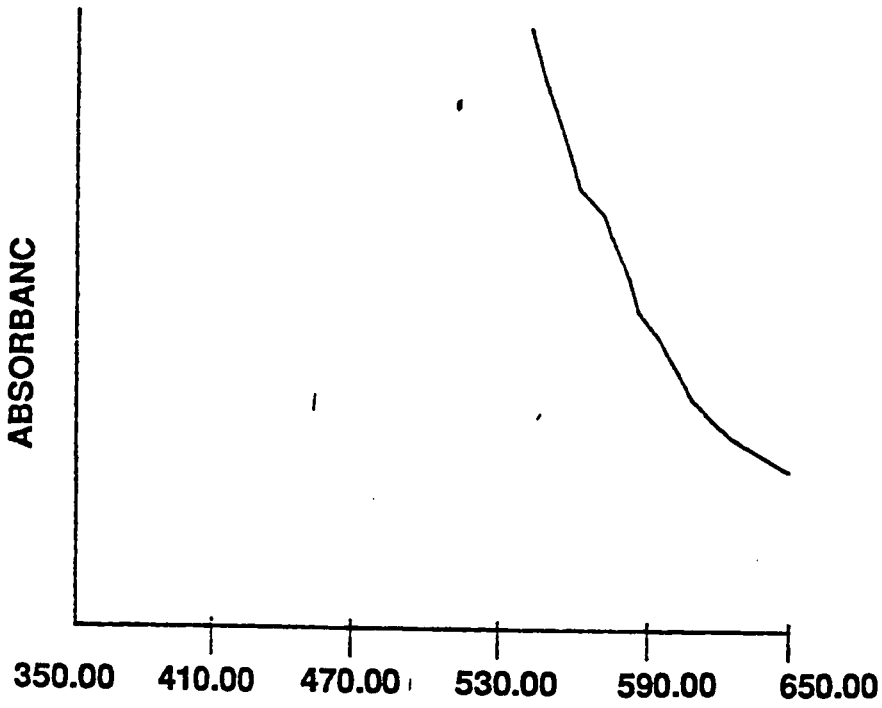


Figure (6) : UV-VIS spectrum of Arab heavy residue GLC eluate by 3:7 $CHCl_3$/n-hexane

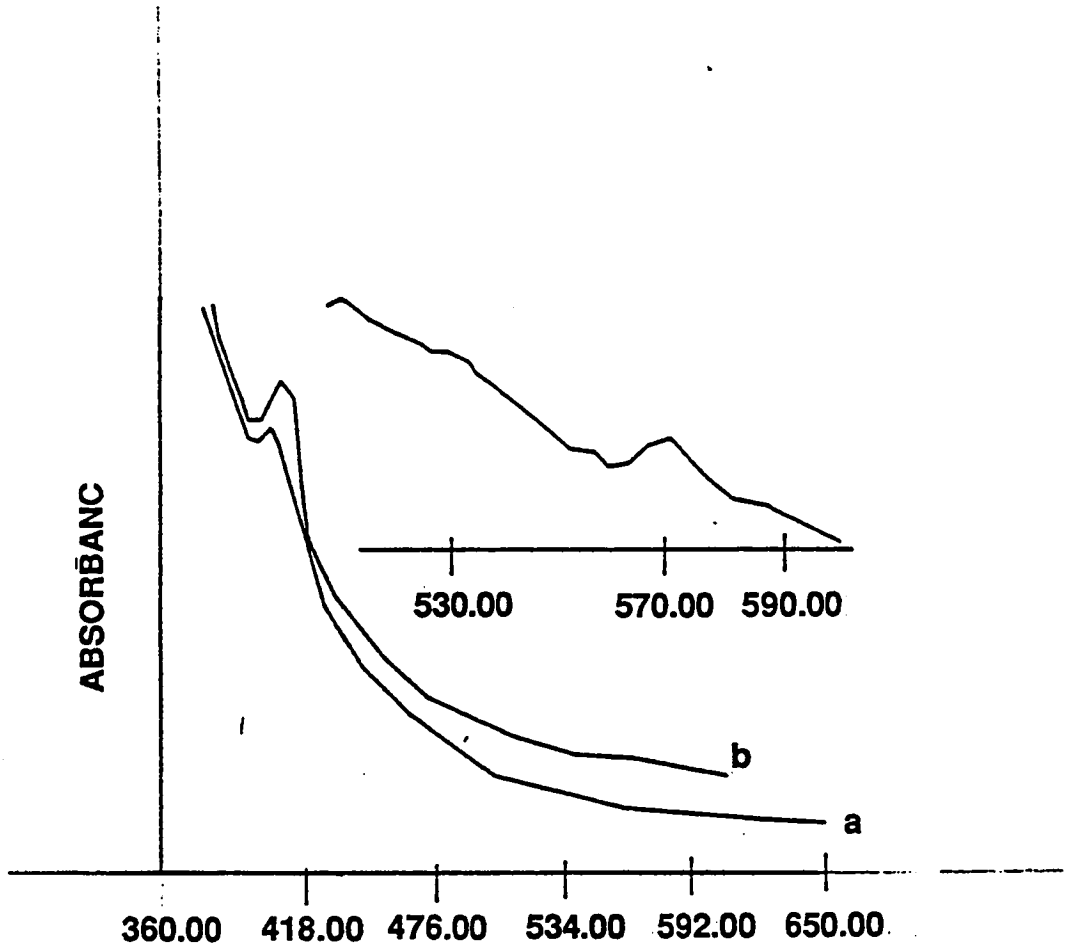


Figure (7) : UV-VIS spectra of (a) 1:1 CH_2Cl_2 /n-hexane eluate from AH residue and (b) fraction after TLC purification.

the low concentration of the nickel in the sample. Therefore, it was decided to investigate for nickel and vanadyl porphyrins in the asphaltenes that was precipitated from the residue cut by n-heptane.

4.2.4- Method No. 4:

The asphaltenes (3.1 grams) obtained by precipitation of the residue cut with n-heptane was chromatographed according to Spencer et al. (27). The DMF eluate (20 wt% of the asphaltenes sample) obtained from the neutral alumina column was extracted in chloroform and adsorbed on silica gel and charged to a glass column containing silica gel (80 grams). It was then eluted with successive solvents of increasing polarity to obtain nickel and vanadyl porphyrins. The fractions eluted with 1:9, 3:7, 1:1, 7:3 v/v chloroform/n-hexane and with chloroform (1.2, 0.8, 0.8, 0.5, and 1 wt% of the asphaltenes sample respectively), all showed weak UV/Vis absorptions at 405, 530,570, and 590 nm (figure 8). These peaks are characteristic of the vanadyl porphyrins.

Also the chloroform extract of the DMF eluate was subjected to thin layer chromatography on an analytical silica gel plate and developed in 1:1 decane=chloroform and showed six different bands. The R_f of which were 0.91-0.96, 0.76-0.91, 0.16-0.76, 0.11-0.16, 0.067-0.11, and 0.044-0.067. The band whose R_f was 0.16-0.76 was the only band showing UV/Vis absorption peaks at 405, 530, 570 and 590 nm which are characteristic of vanadyl porphyrins (figure 9). This method was observed to give relatively better results than the previous methods as far as the UV/Vis absorption is

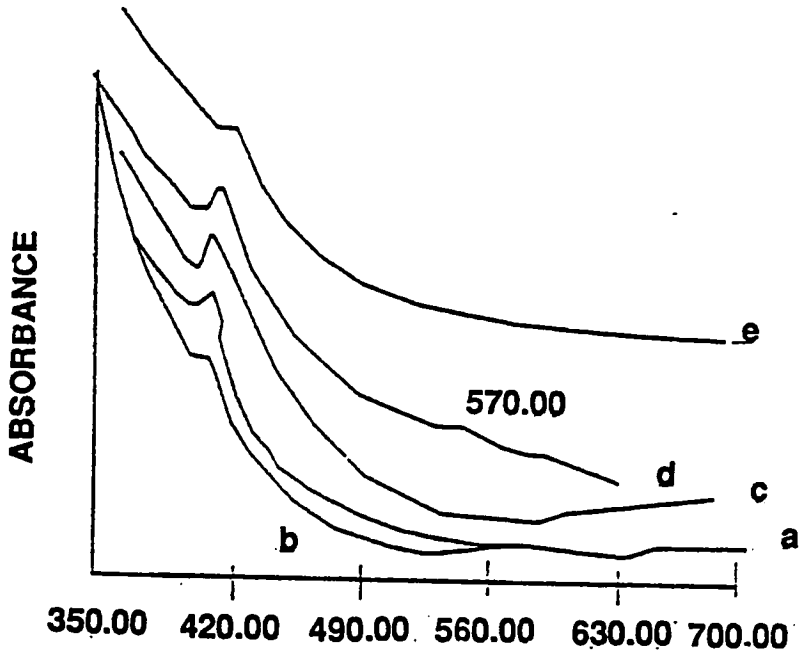


Figure (8) : UV-VIS spectra of GLC fractions from Arab heavy residue asphaltenes by (a) 1:9, (b) 3:7, (c) 1:1 and (d) 7:3 $CHCl_3$ / n-Hexane (e) $CHCl_3$

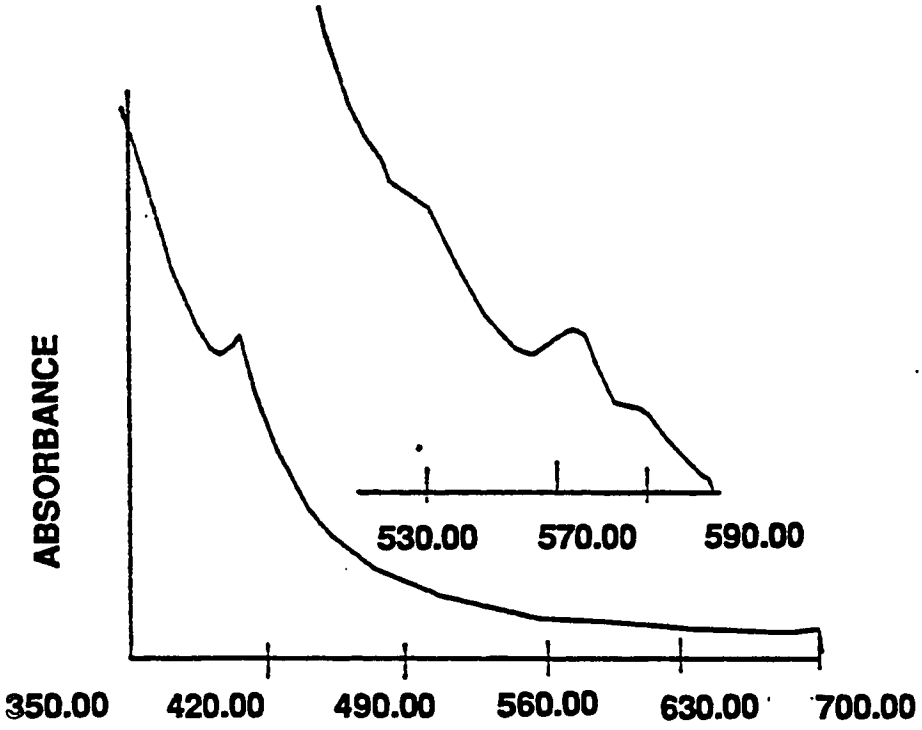


Figure (9) : UV-VIS spectrum of a DMF fraction from residue asphaltenes extrated in chloroform.

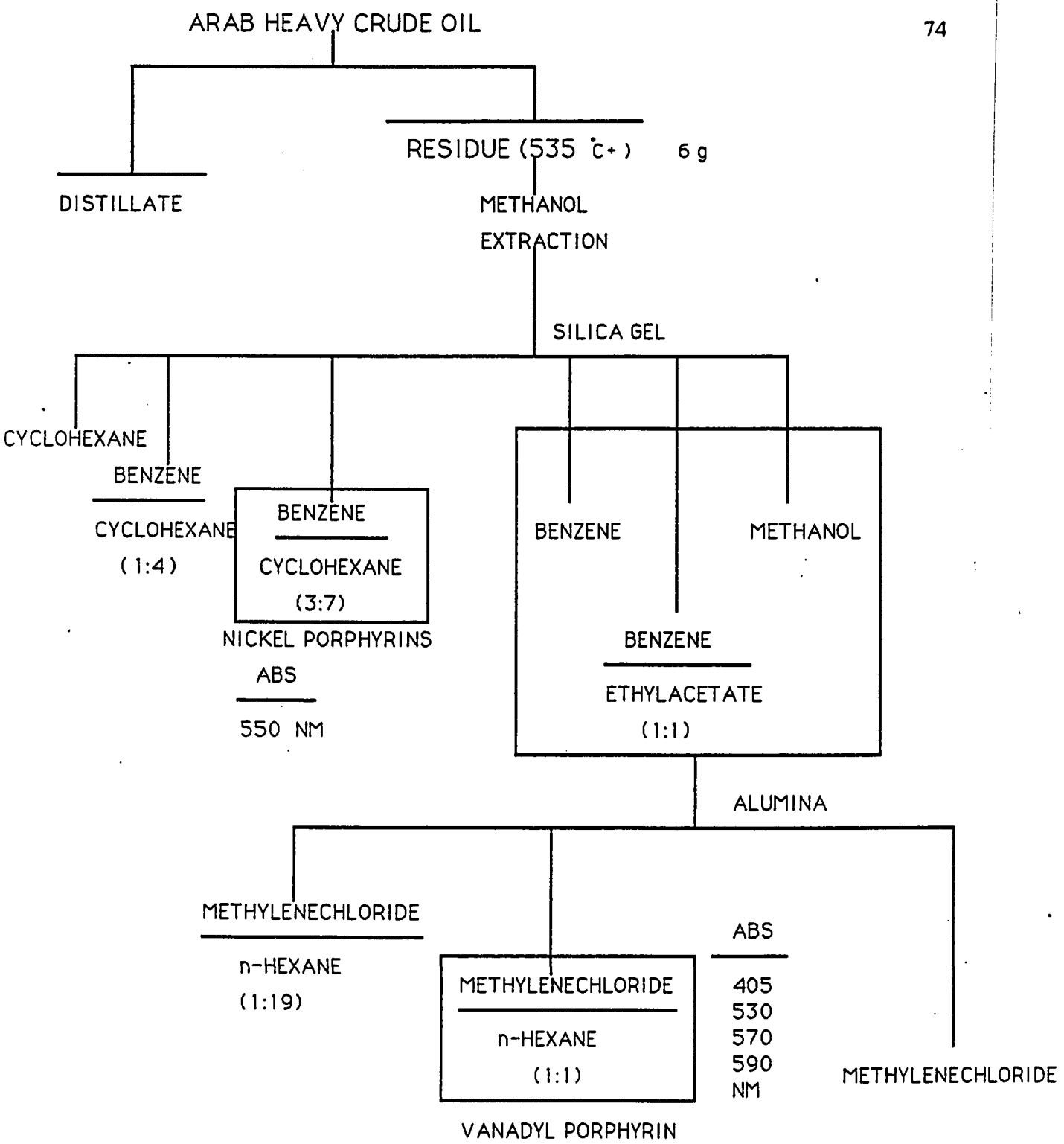
concerned. The background absorption is noticed to be relatively less. However, there was no indication of nickel porphyrins.

4.2.5- Method No. 5:

All the three above mentioned methods of separations were found to give unsatisfactory results. The weak absorptions of the metalloporphyris could result from the high contaminations associated with the separated porphyrins causing high background absorptions which masked the metalloporphyrins UV/Vis absorptions. Because of these unsatisfactory results and the failure to detect any of the nickel porphyrins in the sample, another method was tried.

Combination of HajIbrahim's method (9) and the method developed by Chakraborty and Bhatia, (42) which was used earlier for the separation of nickel and vanadyl porphyrins from the residue cut, was used with some modifications. The solvent sequence is shown in Scheme No. 1. The metalloporphyrin aggregates extracted with methanol were eluted from a silica gel column with, cyclohexane, benzene/cyclohexane (1:4 and 3:7), benzene, benzene/ethylacetate (1:1), and methanol. The weight percentages of these eluates, calculated with respect to the residue sample, were 48, 2, 5, 8, and 3 respectively.

UV/Vis analysis of the above fractions indicated that no absorption peaks were detected for the 1:4 benzene/cyclohexane eluate. A weak absorption band at 550 nm which is characteristic of nickel porphyrins was



Scheme No. 1: Separation of nickel and vanadyl porphyrins from Arab Heavy crude oil residue

detected in the 3:7 benzene/cyclohexane eluate (figure 10). UV/Vis absorption bands at 405, 530, 570, and 590 were detected for the last three eluates, benzene, 1:1 benzene/ethylacetate, and methanol (figure 11). This indicates that the third eluate contained nickel porphyrins only while the last three eluates contained vanadyl porphyrins as can be observed from figures 10 & 11.

The fraction containing the nickel porphyrins was subjected to thin layer chromatography purification on silica gel plate which was developed in 1/1 acetone/n-heptane. The three bands detected: top, middle, and bottom, had R_f values of 0.46-0.69, 0.31-0.46, and 0.023-0.31. Each was scraped off and extracted in methylene chloride and then analyzed by UV/Vis spectrophotometer. The three TLC bands showed no absorption bands for nickel porphyrins. Chakraborty and Bhatia (42) have noticed this phenomenon and attributed it to the lability of nickel porphyrins as compared to the vanadyl porphyrins. They, therefore, explained that the nickel porphyrins decomposed on silica gel.

The last three eluates (benzene, 1:1 ethylacetate/benzene, and methanol) were combined and further purified by chromatographing through alumina (80-200 mesh) column. The column was eluted with 1:19 cyclohexane/benzene, 1:1 methylene chloride/n-hexane, and methylene chloride. The calculated weight percentage yields on residue were 3%, 0.5%, and 2%. The second eluate (1:1 methylenechloride/n-hexane) was of a red color and gave strongly resolved UV/Vis absorption peaks, which were characteristic of vanadyl porphyrins, at 405, 530, 570, and a shoulder at 590

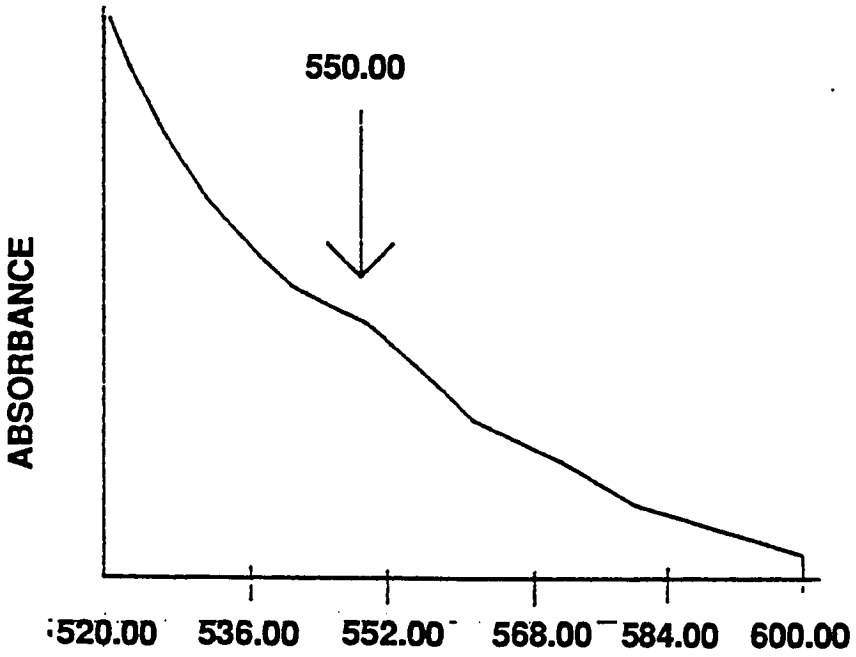


Figure (10) : UV-VIS spectrum of nickel porphyrins from Arab heavy residue.

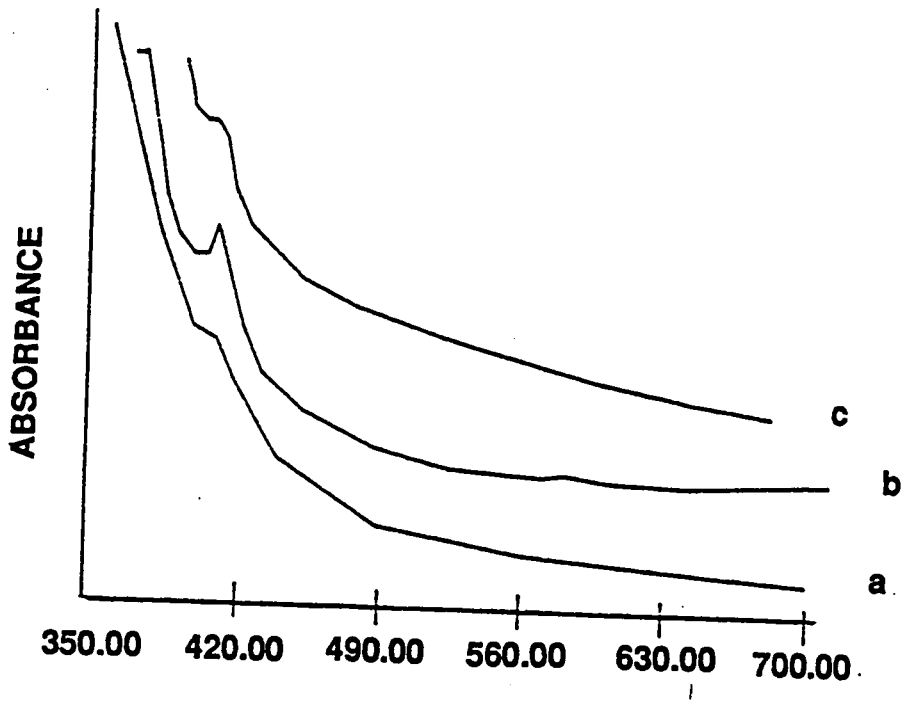


Figure (11) : UV-VIS spectra of (a) benzene eluate, (b) 1:1 benzene/ethyl acetate eluate and (c) ethyl acetate eluate.

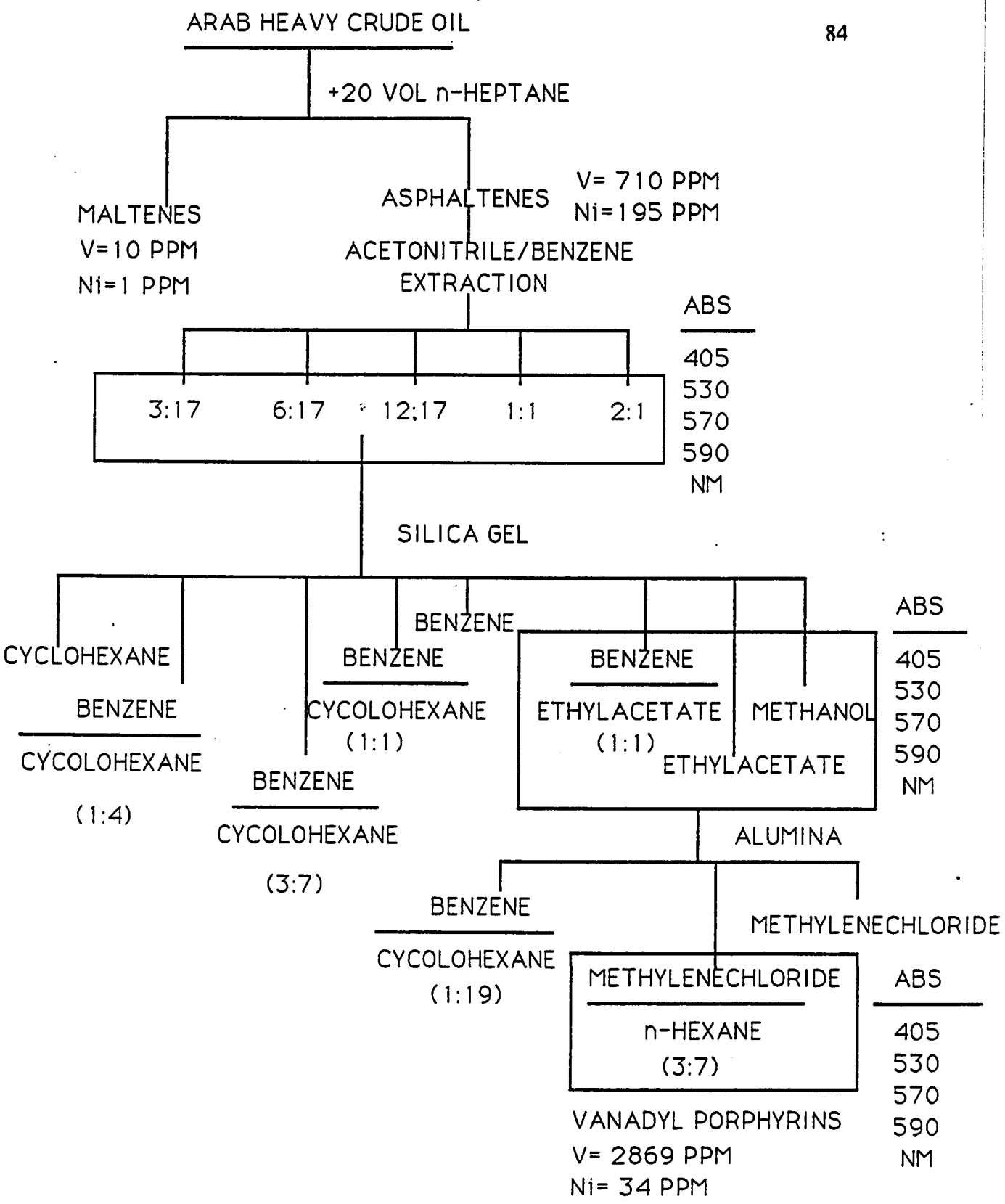
nm (figure 12). The XRF analysis showed 534 ppm vanadium and traces of nickel. The other two eluates showed no porphyrinic absorption bands.

The isolated vanadyl porphyrins were subjected to a thin layer chromatographic study. The sample was dissolved in a minimum amount of methylene chloride and charged by means of a capillary tube to an analytical silica gel plate, which was activated at 110°C for half an hour and developed in chloroform/decane (1:1). Five bands were observed. One of which had a red color, characteristic of vanadyl porphyrins, and had an R_f of 0.54-0.69. This band when scraped off and extracted with methylene chloride showed UV/Vis absorption peak at 405, 530, 570, and a shoulder at 590 nm (figure 13). The other bands had R_f values of 0.00-0.54, 0.69-0.84, 0.84-0.89, 0.89-0.94 respectively and did not show any porphyrinic absorptions.

4.2.6- Method No. 6:

Separation of Nickel & Vanadyl Porphyrins from Crude Oil Asphaltenes:

Asphaltenes (10 grams) that were already precipitated by n-heptane from Arabian Heavy crude was extracted in Soxhlet by solvents of successively increasing proportions of benzene in acetonitrile. Each extraction was continued till the extracting solvent remained colorless. The extraction process was monitored by UV/Vis spectrophotometer, and it was discontinued when the UV/Vis absorption band at 405 nm had diminished (figure 14). All of the extracts (3:17, 6:17, 12:17, 1:1, 2:1 v/v of benzene/acetonitrile) showed



Scheme No. 2: Separation of nickel and vanadyl porphyrins from Arab Heavy crude oil asphaltenes

methylene chloride/n-hexane (3:7) (0.20% w.r.t. asphaltenes sample) and with methylene chloride (0.20 and 0.07 wt% of the asphaltenes sample respectively) were red in color and had intense UV/Vis absorption bands at 405, 530, 570 nm and a shoulder at 590 nm (figure 15). These fractions, therefore, were mixed together for further TLC purification and identification studies.

The vanadyl porphyrins sample was introduced to a thin layer silica gel analytical plate and developed in decane/chloroform (1:1). Four bands were observed. The R_f values of which were 0.00-0.48, 0.48-0.63, 0.63-0.85, and 0.85-0.91. The band whose R_f was 0.48-0.63 was red in color. This layer was removed and extracted in methylene chloride. The UV/Vis analysis of which showed very resolved peaks at 405, 530, 570 nm and a shoulder at 590 nm (figure 16).

The model compound vanadyl(IV) etioporphyrin III (STREM Chemicals, U.S.A.) was subjected to a thin layer chromatographic analysis under similar conditions. A spot was observed to move upward along the plate. The R_f of which was 0.59. It can be noted that the R_f value (0.59) of the model compound was within the R_f value of the red band observed for the vanadyl porphyrins separated from the Arabian Heavy asphaltenes and the residues. Further, it may be concluded that the vanadyl compounds present in Arabian Heavy samples are not a single type of compounds. The R_f values of the separated vanadyl porphyrins and the model compound are compared (see

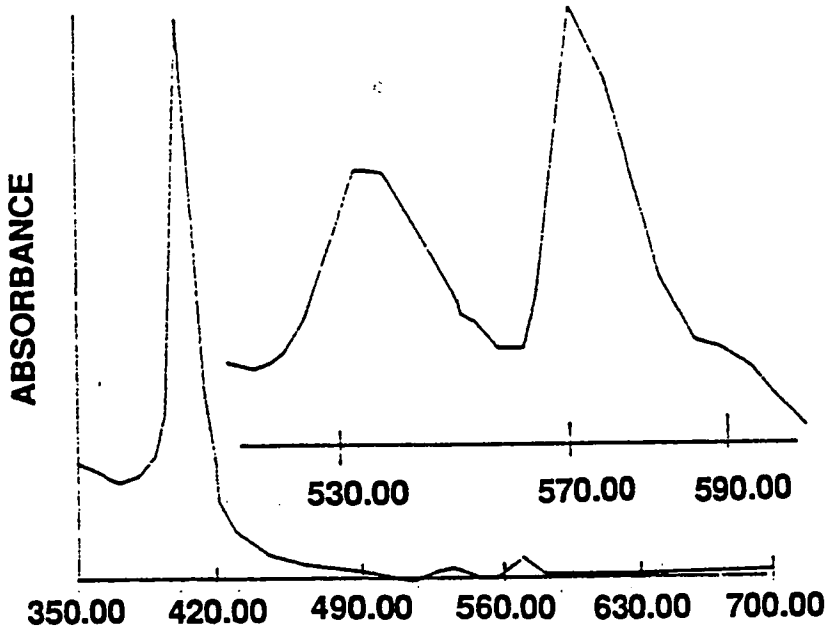


Figure (15) : UV-VIS spectrum of vanadyl porphyrins from Arab heavy asphaltenes.

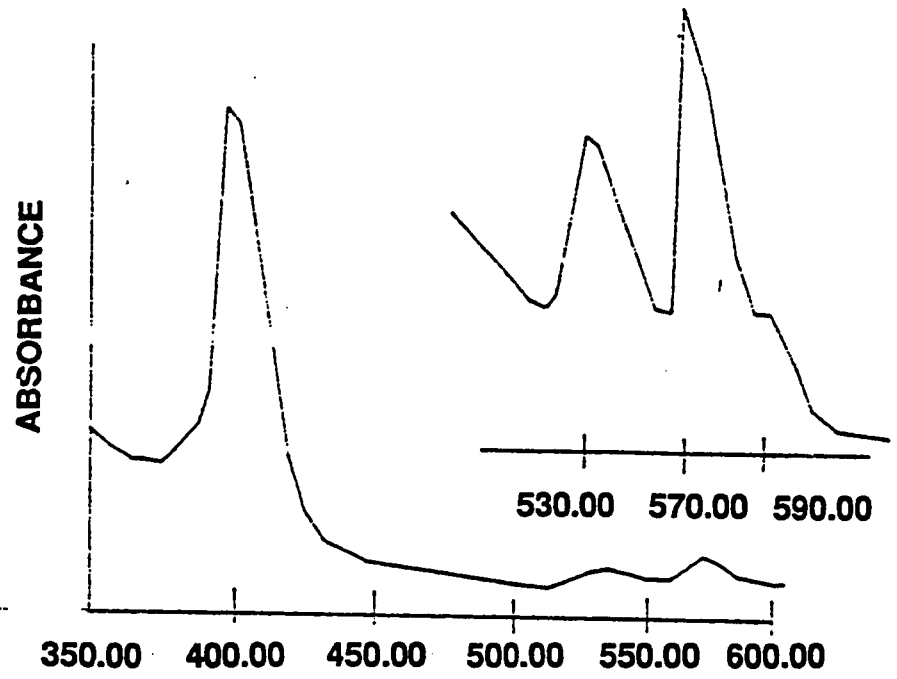


Figure (16) :UV-VIS spectrum of TLC fraction of vanadyl porphyrins from Arab heavy asphaltenes.

table 4).

4.3- High Performance Liquid Chromatography (HPLC) Fingerprinting

High performance liquid chromatography is a powerful technique used for separation as well as for fingerprinting in the field of metallopetroporphyrins.

Separation of vanadyl petroporphyrins obtained from Arabian Heavy oil residues and asphaltenes by HPLC on a reverse phase column had indicated the presence of a mixture of compounds and/or isomers.

The retention times increase with the number of carbon atoms in the lateral chains of the vanadyl porphyrins of individual compound groups(18). In addition, the deoxophylleoerythroetioporphyrin (DPEP) series were found to be more strongly retained in such a column than were the etioporphyrin (Etio) series. Therefore, the Etio series were generally observed to elute before the DPEP series (18, 19, 23, 24) .

Water Associates high performance liquid chromatography instrument was used for fingerprinting purposes. Different conditions (isocratic and gradient elutions through a shorter and a relatively longer column) were tried in order to obtain satisfactory separations.

4.3.1- Condition A:

The HPLC method developed by Sundraraman (26) was modified, using 5 μ columns (Water Associates Product, 25 cm x 0.46 mm) instead of 3 μ

Table 4- R_f Values of Isolated and Model Vanadyl Porphyrins

Sample origin	R_f*
Residue	0.54 - 0.69
Asphaltenes	0.48 - 0.69
Model Compound	0.59

* Measured in decane/chloroform (1:1)

(Hypersil) but with the same solvent system of 45% CH_3OH, 45% CH_3CN and 10% H_2O at the same flow rate of 1 ml/min, a hump with very weak peaks started to elute at retention time of ca. 6 min. and ending at ca. 20 min. was observed for the vanadyl porphyrins separated from the Arabian Heavy crude asphaltenes (figure 17).

4.3.2- Condition B:

A linear gradient solvent program was tried using 100% of the mixture, which was used in condition A, as solvent A going to 100% of a mixture of 50% CH_3OH and 50% CH_3CN as solvent B in 40 min., the same pattern as in condition A was observed (figure 18).

4.3.3- Condition C:

However, when the system was reversed from a mixture of 50% CH_3OH, and 50% CH_3CN as solvent A to 100% of a mixture of 45% CH_3OH, 45% CH_3CN, and 10% H_2O as solvent B, the peaks started to show up at a longer retention time (ca. 10 min.) than in condition A and in a single but a narrower hump (figure 19).

4.3.4- Condition D:

When an isocratic run was tried using methanol at 1 ml/min, a hump was observed forming one main relatively broad peak at ca. 13 min. and two shoulder peaks at a longer retention time of 11.5 min. and one shoulder at a

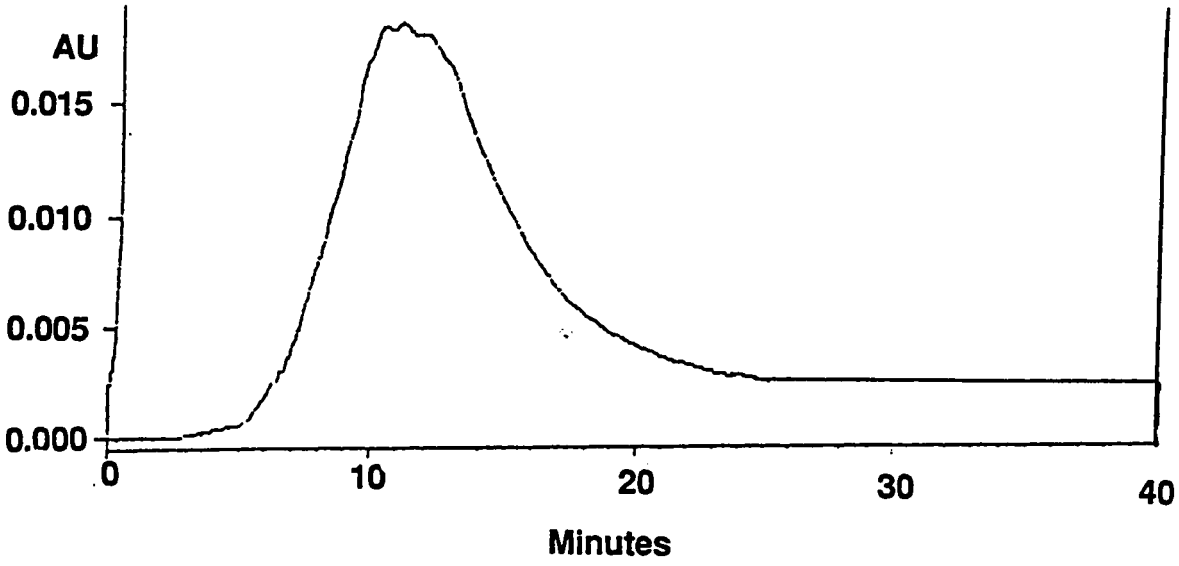


Figure (17) : HPLC of vandadyl porphyrins from AH asphaltene : isocratic elution : (45% CH_3OH, 45% CH_3CN, 10% H_2O) : C18 column (25 cm x 0.46 mm)

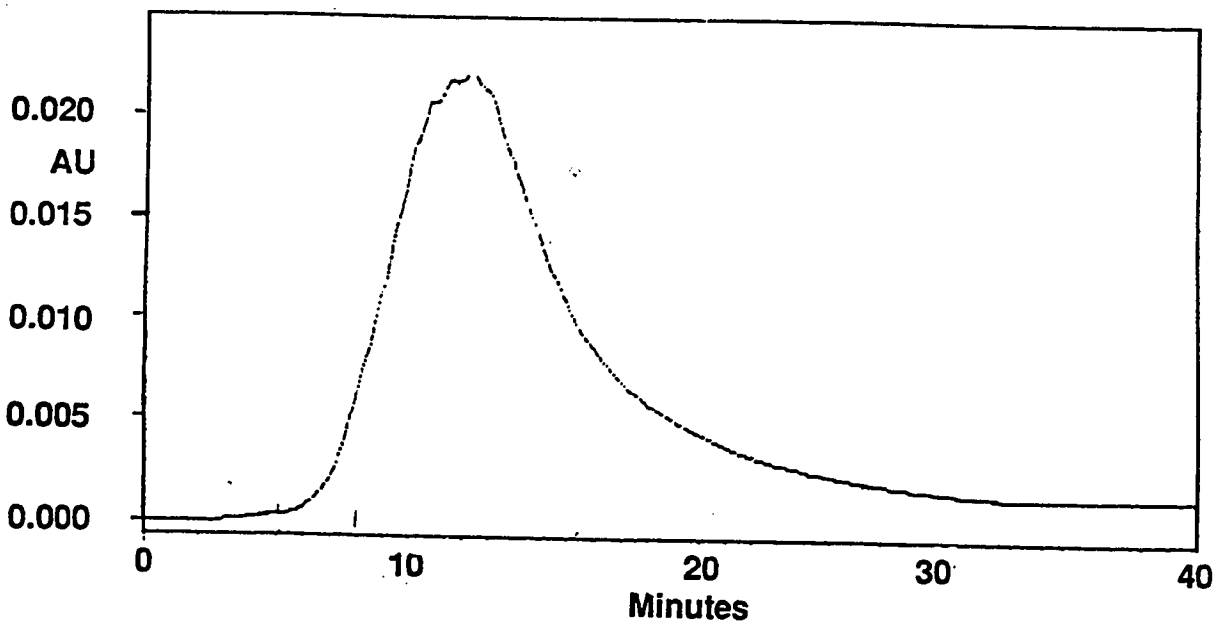


Figure (18) : HPLC of vanadyl porphyrins from AH asphaltens : linear gradient elution of A (45% CH_3OH, 45% CH_3CN, 10% H_2O) to B (50% CH_3OH, 50% CH_3CN) : C18 column (25 cm x 0.46 mm)

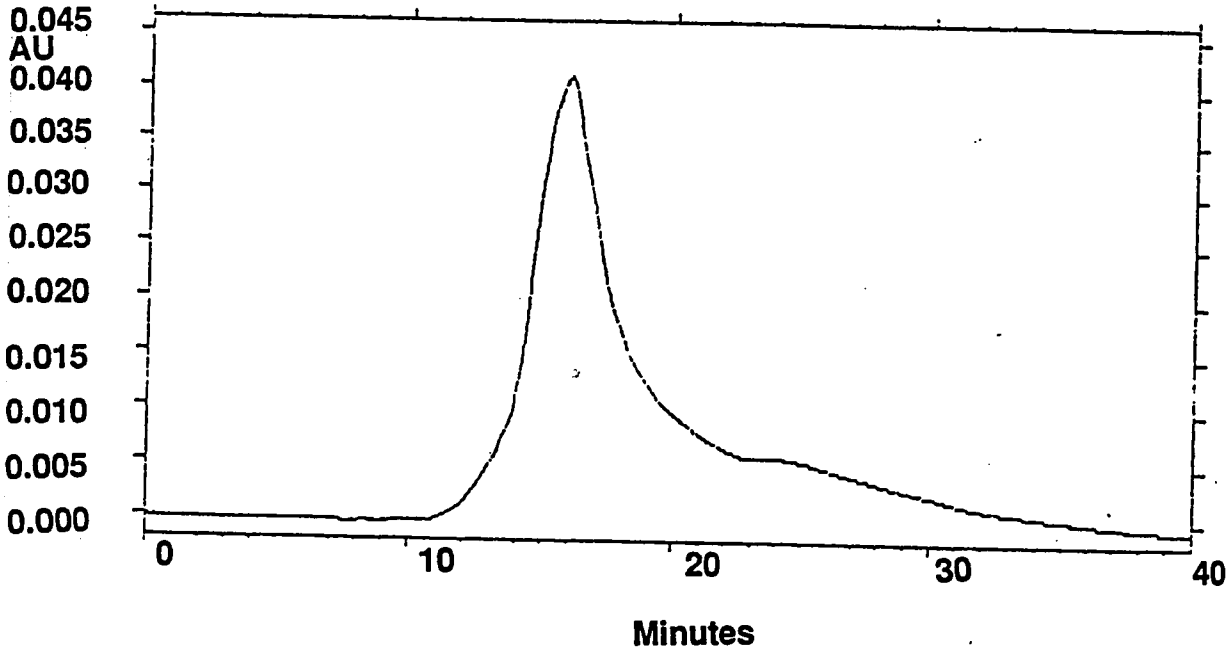


Figure (19) : HPLC of vanadyl porphyrins linear gradient elution A (50% CH_3OH, 50% CH_3CN) going to B (45% CH_3OH, 45% CH_3CN, 10% H O) : C18 column (25 cm x 0.46 mm)

shorter retention time of 15 min.. In addition, a very small peak at ca. 6 min was detected (figure 20).

The resolution obtained so far was not satisfactory; therefore, it was decided to increase the column length by joining two-5 μ C-18 columns (25 cm x 0.46 mm each) together.

4.3.5- Condition E:

Gradient linear elution of 70% methanol and 30% of a mixture of 40% CH_3OH, 40% CH_3CN, and 20% water as solvent A going to 30% of the methanol and 70% of the mixture as solvent B was performed. A more resolved peak at ca. 13 min. and a small broad peak at ca. 18 min. and a relatively smaller sharp peak at 11.3 min. were observed (figure 21).

4.3.6- Condition F:

When an isocratic system of 5 % chloroform in methanol was used (19,20,23) in our system of two-5 micron C-18 columns, the vanadyl porphyrins from asphaltenes of the Arabian Heavy crude was separated into three well resolved peaks. Two major peaks at 12 min. and 14 min. were observed. A third peak at 10 min. and a shoulder at ca. 9 min. were detected. The retention times were observed to be less than in condition E (figure 22).

4.3.7- Condition G:

Isocratic elution of only MeOH was tried using the above two column

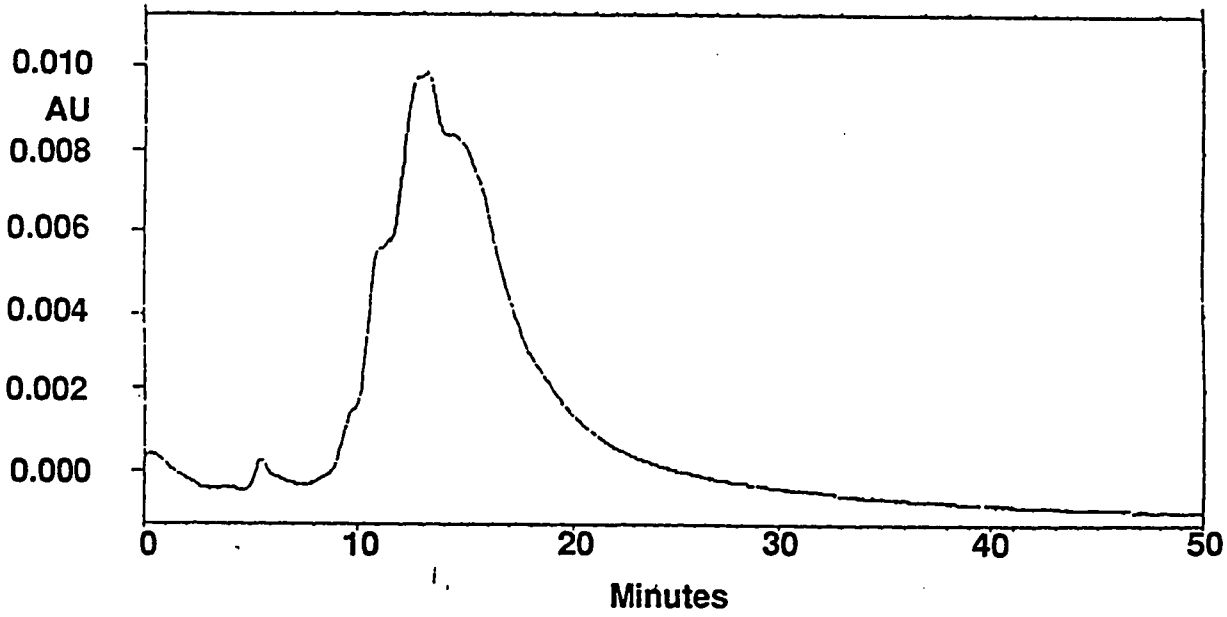


Figure (20) : HPLC of vanadyl porphrins from AH asphaltenes: isocratic elution : MeOH, Cl8 column (25cm x 0.46mm)

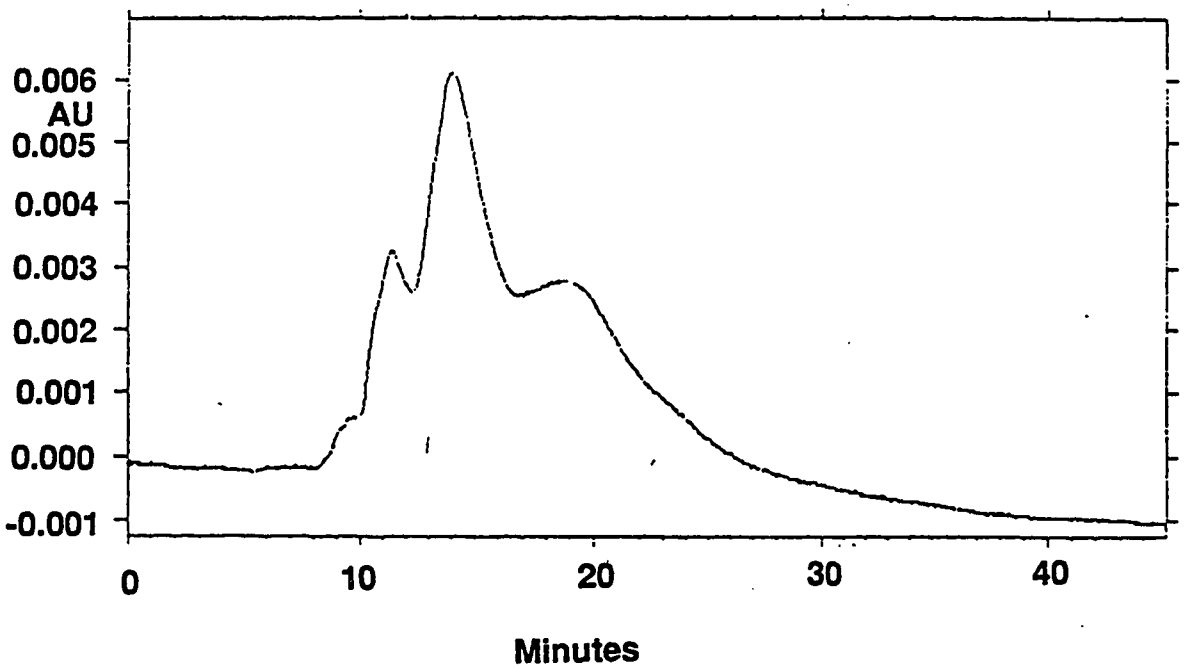


Figure (21) : HPLC of Vanadyl porphyrins from AH asphaltenes : Linear gradient : from 30% of (40% CH_3OH; 40%, CH_3CN ; 20% H_2O) and 70% MeOH going to 70% (40% CH_3OH, 40% CH_3CN, 20% H_2O) and 30% MeOH, 2 C18 column (25 cm x 0.46 mm).

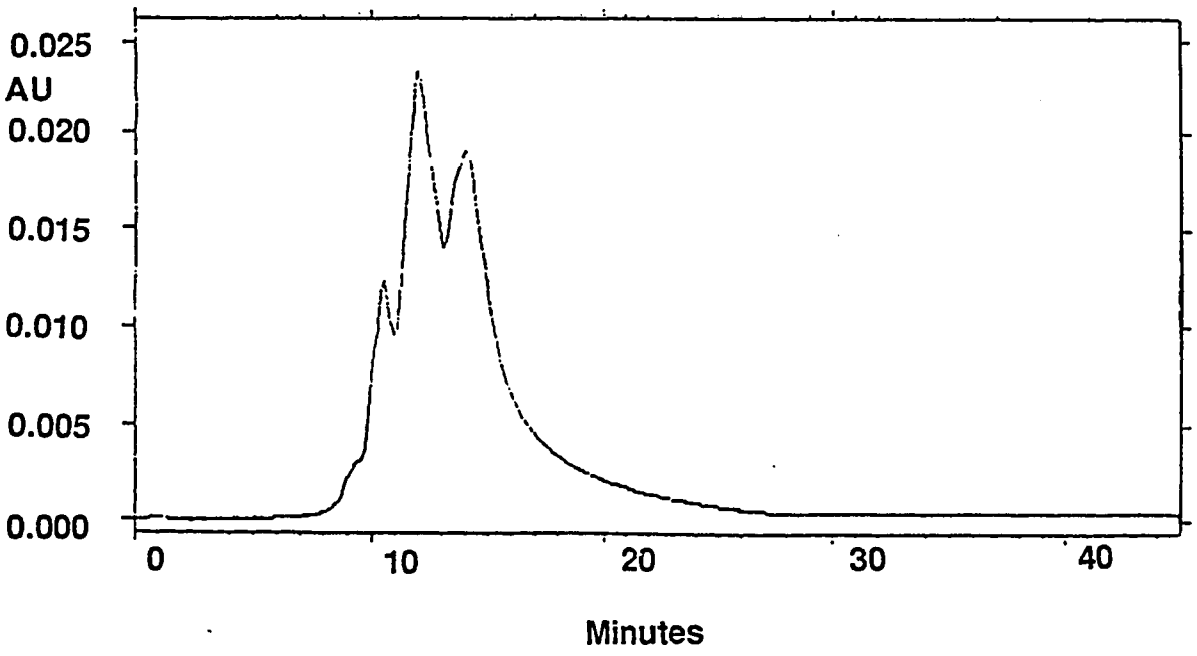


Figure (22) : HPLC of vanadyl porphyrins from AH asphaltenes : isocratic elution : 5% $CHCl_3$/MeOH, 2 Cl8 column (25 cm x 0.46 mm)

system and the same sample. Three main peaks at 13.5, 16.0, and 19.5 min. were detected respectively. Three shoulders at 14.5, 16.5, and 21.0 min. were detected in addition to a fourth small one at 12.5 min. Retention times were observed to be longer than it was in condition F (figure 23). A standard vanadyl porphyrin compound of C_{32} Etio (III) was run under similar conditions as in condition G. One peak was observed at 12.6 min. (figure 24) which indicates that the standard reference compound is likely to be present in vanadyl porphyrin mixture separated from the Arabian Heavy crude's asphaltenes.

Vanadyl porphyrins, which were separated from Arabian Heavy crude's asphaltenes, were subjected to TLC and the vanadyl porphyrin TLC band was fingerprinted by HPLC using the same two C-18 columns and methanol as the eluting solvent. One main peak at 11.5 min. and a shoulder at a longer retention time of 12 min appeared. Two other peaks were detected at 10.5 min. and 14 min (figure 25). This HPLC profile also indicated the probable presence of the C_{32} Etio (III) vanadyl porphyrins.

The HPLC behavior of the vanadyl porphyrins isolated from the residue of the Arabian Heavy crude can be seen in figure 26. Two main peaks, small peak, and a shoulder were detected at 10, 12, 17, and 9 min. respectively. Based on the retention time of the standard compound measured under similar conditions, the residue vanadyl porphyrins may contain C_{32} Etio (III) vanadyl porphyrin as one of its components.

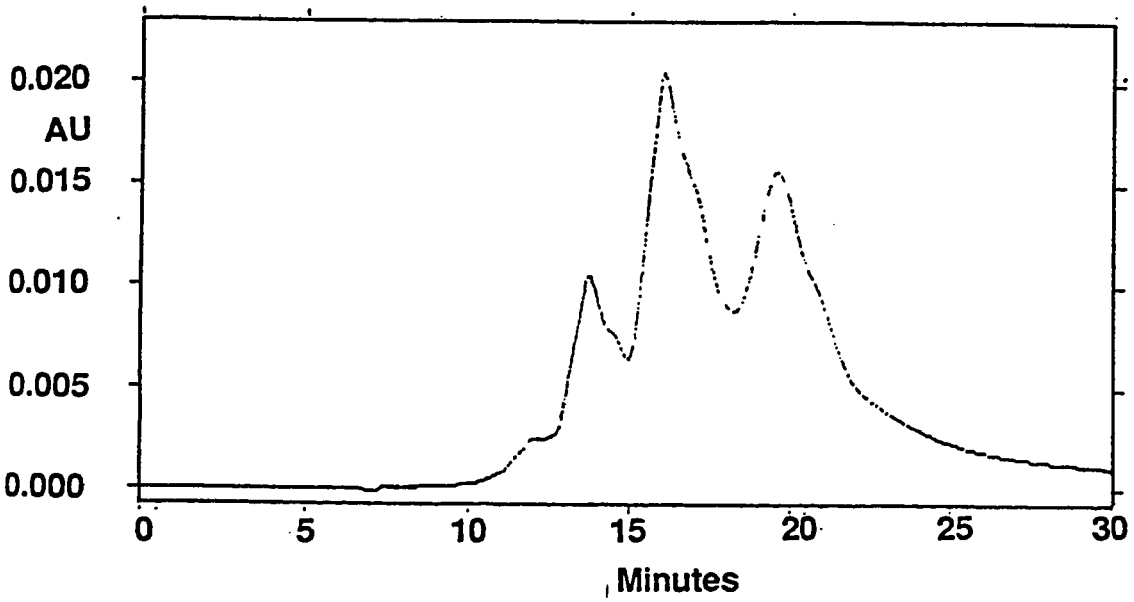


Figure (23) : HPLC of vandadyl porphyrins from AH asphaltenes isocratic elution : MeOH, 2 C18 column (25 cm x 0.46 mm)

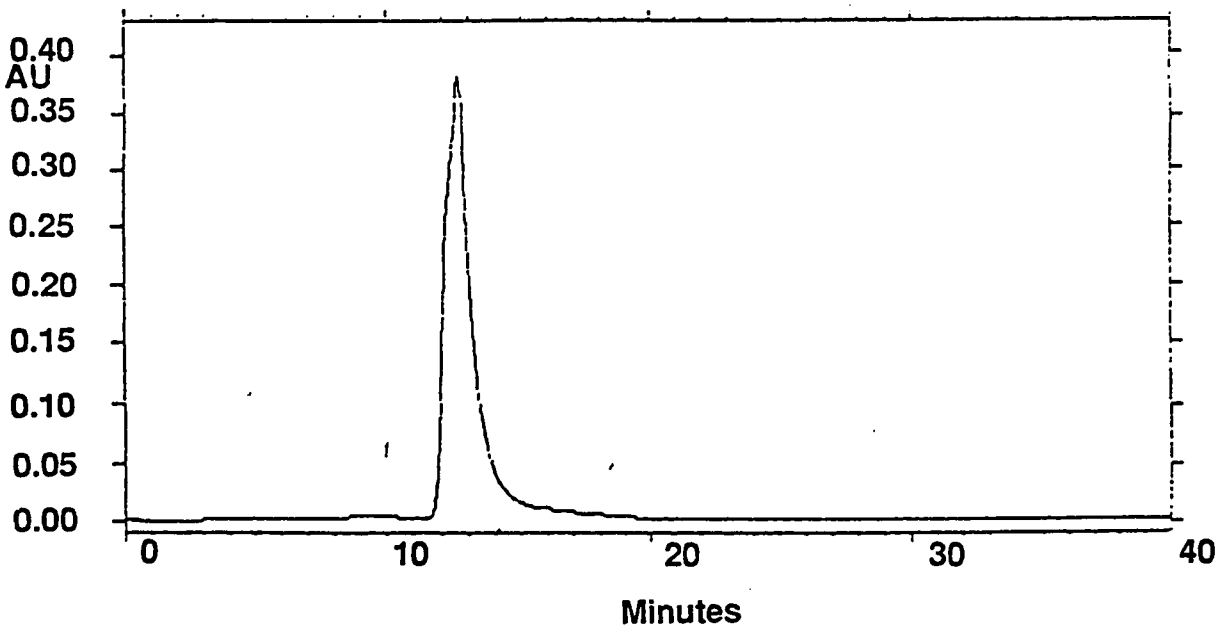


Figure (24) : HPLC of standard vanadyl porphyrin (III) isocratic elution : MeOH, 2 Cl8 column (25 cm x 0.46 mm)

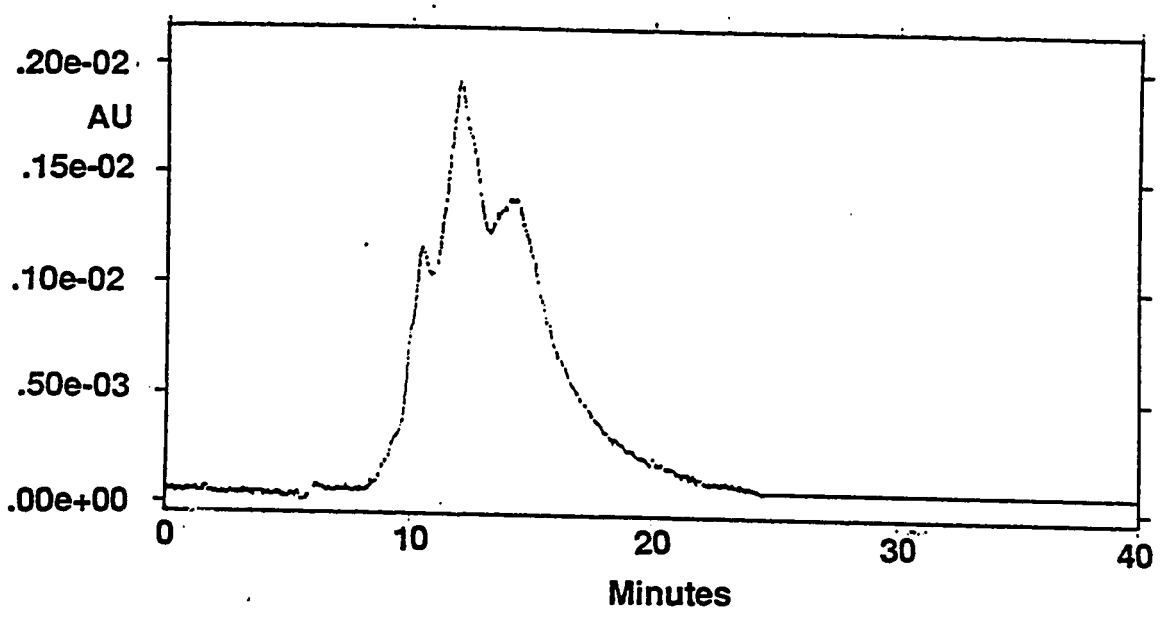


Figure (25) : HPLC of vandadyl porphyrins (TIC band) from AH asphaltenes, isocratic elution : MeOH, 2 C18 column (25 cm x 0.46 mm)

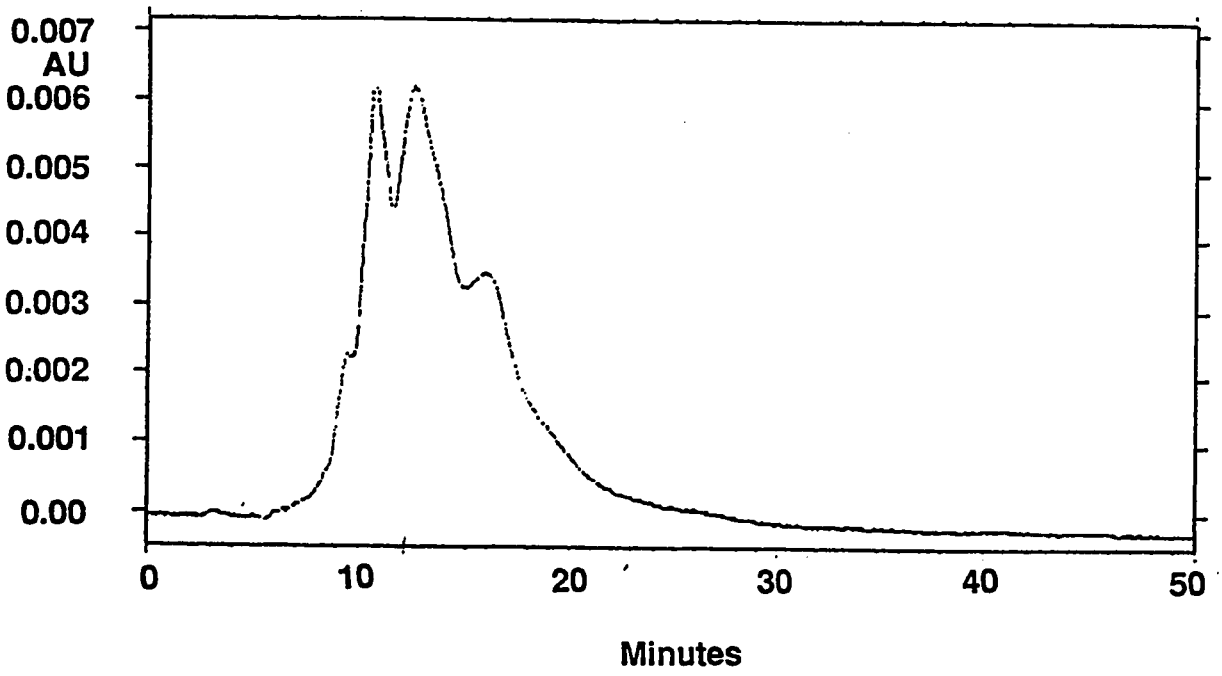


Figure (26) : HPLC of vandadyl porphyrins from AH residue, isocratic elution : MeOH, 2 Cl8 column (25 cm x 0.46 mm)

The HPLC profile of the vanadyl porphyrins separated from the residue was noticed to be different from the HPLC profile of the vanadyl porphyrins separated from asphaltenes (see figures 24 & 26). This suggested that they were either different types of vanadyl porphyrins or the relative amounts of each type was different in the residue and asphaltenes. The mass spectra analysis of which (as will be discussed later) showed that the residue and asphaltenes contained the same types of vanadyl porphyrins but the relative amount of each type was different. The DPEP type was predominating in asphaltenes, where the Etio was predominating in the residue cut.

The HPLC profile of the TLC band of the residue vanadyl porphyrins is shown in figure 27. It could be observed that the profile was different than that of the vanadyl porphyrins from the residue before it was subjected to TLC (compare figures 26 & 27). However, the HPLC pattern was similar to that of the TLC band of the vanadyl porphyrins from asphaltenes (compare figures 25 & 27). One main peak at 11 min. and two other peaks at 9.5 and 13 min. respectively were detected in addition to a shoulder at 8.5 min (figure 27). The similarity of the HPLC profiles of the TLC vanadyl porphyrins bands from residue and asphaltenes could be explained on the basis that TLC selectively separated certain types of vanadyl porphyrins.

4.4- Mass Spectrometric measurements:

The use of mass spectrometry in the field of metallopetroporphyrins is recent. Especially, the low voltage mass spectrum is the heart of the characterization techniques of metallopetroporphyrins. The low volatility of

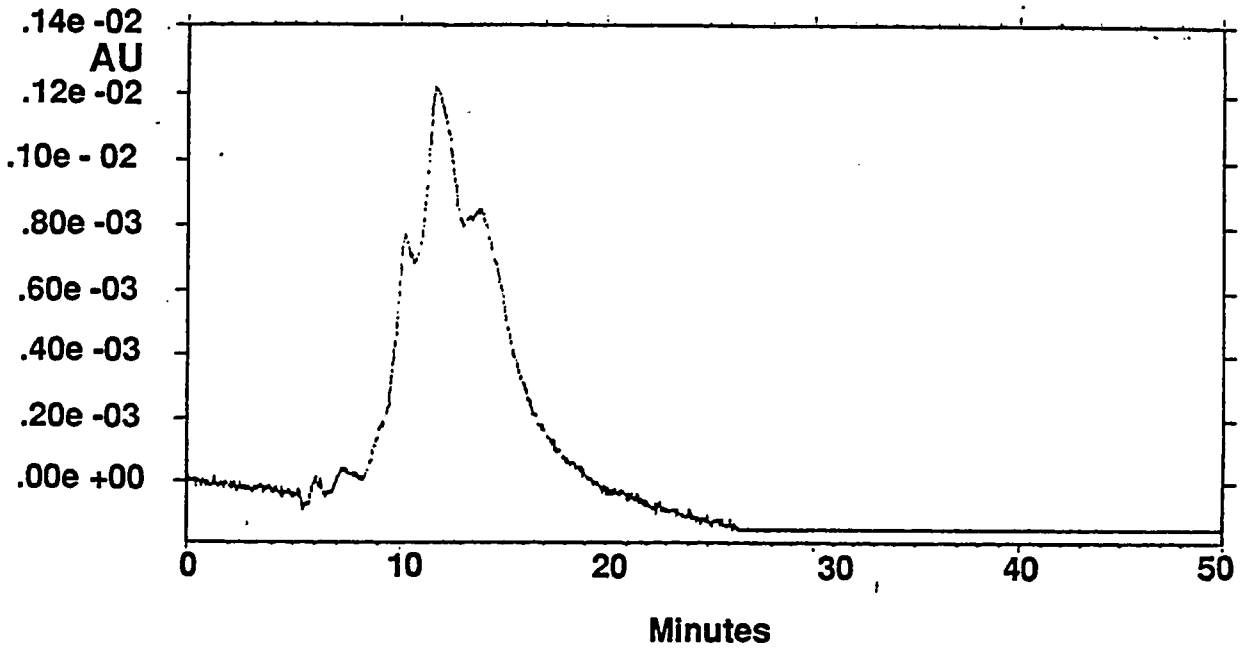


Figure (27) : HPLC of vandadyl porphyrin (TLC band) form AH residue isocratic elution : MeOH, 2 Cl8 column (25cm x 0.46 mm)

porphyrins or metalloporphyrins necessitates the use of a spectrometer with a direct solid sample injection probe so that the sample is directly introduced to the ionizing beam.

Baker et al. have recommended that mass spectra of fossil porphyrins be measured at 260°C probe temperature (62). We, however, have modified it and measured our separated vanadyl porphyrins at a programmed temperature from 70 - 350°C at 16°C/min. The voltage used (18 eV) was very low to minimize further fragmentation and to get mainly the molecular peaks.

The total ion chromatogram (TIC) profiles have indicated that the bulk of the vanadyl porphyrins were pyrolyzed after 11 - 15 minutes of mass measurement (figures 28 &29). This means that the vanadyl porphyrins obtained from both of the residue and the asphaltenes of the Arabian Heavy crude oil can be pyrolyzed at 240 – 310°C. The differential volatilization of the vanadyl porphyrins could be solved by averaging the spectra over the range of the volatility of the sample according to Quirke (14).

The molecular weight of the basic structure of an etioporphyrin molecule incorporating vanadyl (Vanadyl Etio) is 375. The alkyl-substituted series of the molecule evidently corresponds to 375 + 14n where n is an integer value of 1 or greater (M series). Likewise, the vanadyl deoxophylleocrythroetioporphyrin (vanadyl DPEP) series corresponds to 401 + 14n (M - 2 series). The tetrahydrobenzo DPEP series corresponds to 455 + 14n (M - 4 series), where as rhodo Etio (M - 6 series) and rhodo DPEP (M - 8 series) correspond to 425 + 14n and 465 + 14n respectively.

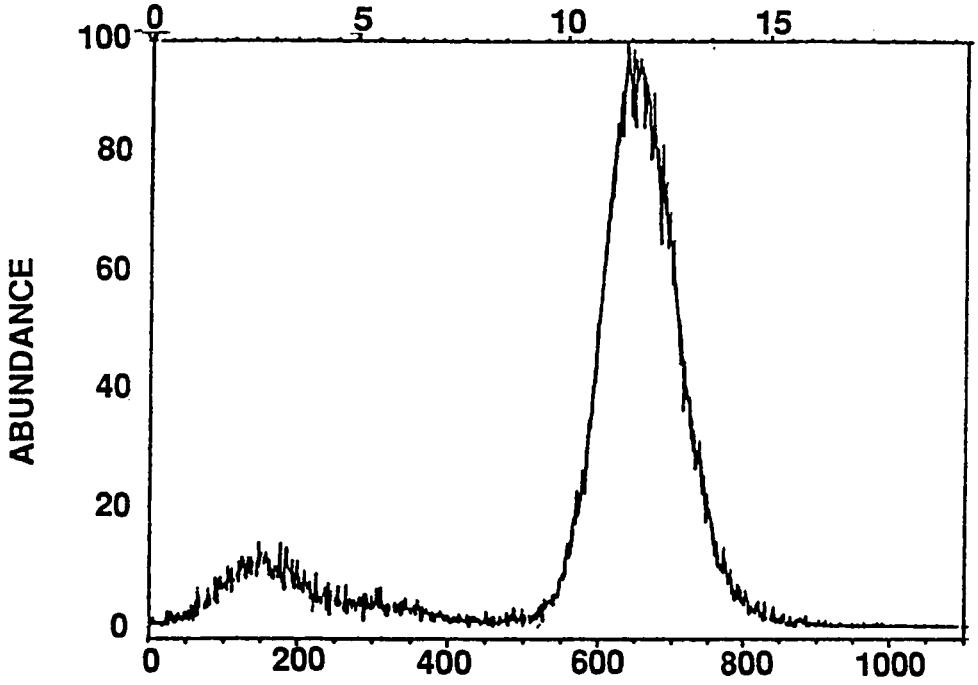


Figure (28) : Total Ion Chromatogram of vanadyl porphyrins from Arab Heavy asphaltenes.

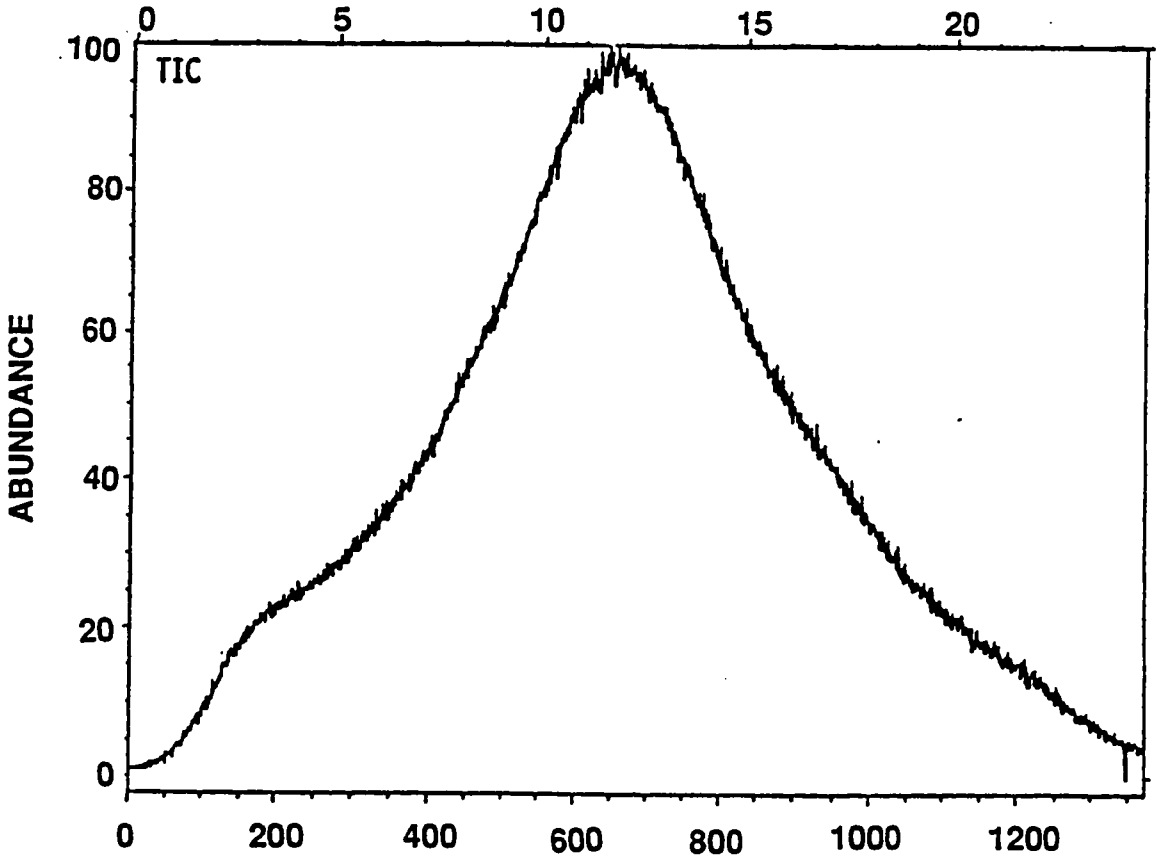


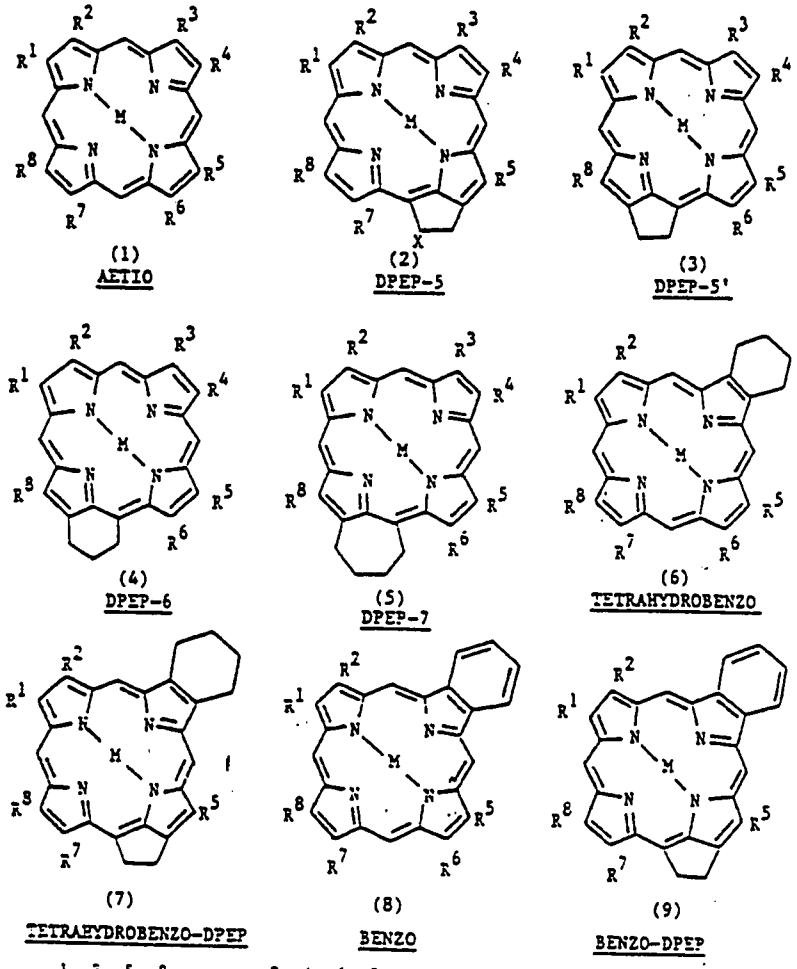
Figure (29) : Total Ion Chromatogram of vanadyl porphyrins from Arab Heavy residue.

Mass spectral analysis of vanadyl porphyrins isolated from both the asphaltenes and residue of Arabian Heavy crude oil indicated that they contained mainly two homologous series of vanadyl DPEP and vanadyl etioporphyrins (M - 2 and M respectively) as well as small amount of M - 4, M - 6, and M - 8 series. Within each series, there were individual compounds that differed in the total number of carbon atoms on the side frame of the porphyrin ring (figure 30). The mass spectra of these vanadyl porphyrins showed that they were very complex mixtures.

The mass spectra of Arabian Heavy residue and asphaltenes vanadyl porphyrins were observed to exhibit a Gaussian-like mass distribution (figures 31, 32). This distribution is characteristic of the petroleum vanadyl porphyrins (62).

The mass spectra of the vanadyl porphyrins isolated from the asphaltenes of the Arabian Heavy indicated that it contained more vanadyl DPEP than Etio. This finding agreed with what Didyk et al. have found (64). It indicated that the asphaltenes preferentially concentrated the vanadyl DPEP due to incorporation of these type of porphyrins into the asphaltic host by forming π - π molecular complexes with the asphaltenes aromatics. In addition, the incorporation of the porphyrins in the asphaltic host was affected by their polarity and thus resulted in the preferential incorporation of the DPEP type porphyrins (64).

Benzo vanadyl porphyrins , basically an alkylbenzo vanadyl porphyrin as was proposed by Baker et al. (62), were found to coexist with the main two



1(a) $R^1,R^3,R^5,R^8 = CH_3$; $R^2,R^4,R^6,R^7 = C_2H_5$
1(b) $R^1,R^3,R^5,R^8 = CH_3$; $R^2,R^4,R^7 = C_2H_5$; $R^6 = H$
2(a) $R^1,R^3,R^5,R^8 = CH_3$; $R^2,R^4,R^7 = C_2H_5$; X = OH
2(b) $R^1,R^3,R^5,R^8 = CH_3$; $R^2,R^4,R^7 = C_2H_5$; X = H
2(c) $R^1,R^3,R^5,R^8 = CH_3$; $R^2,R^4 = C_2H_5$; $R^7 = CH_2CH_2CO_2H$; X = H

Figure (30) : Strucure of geoporphyrins

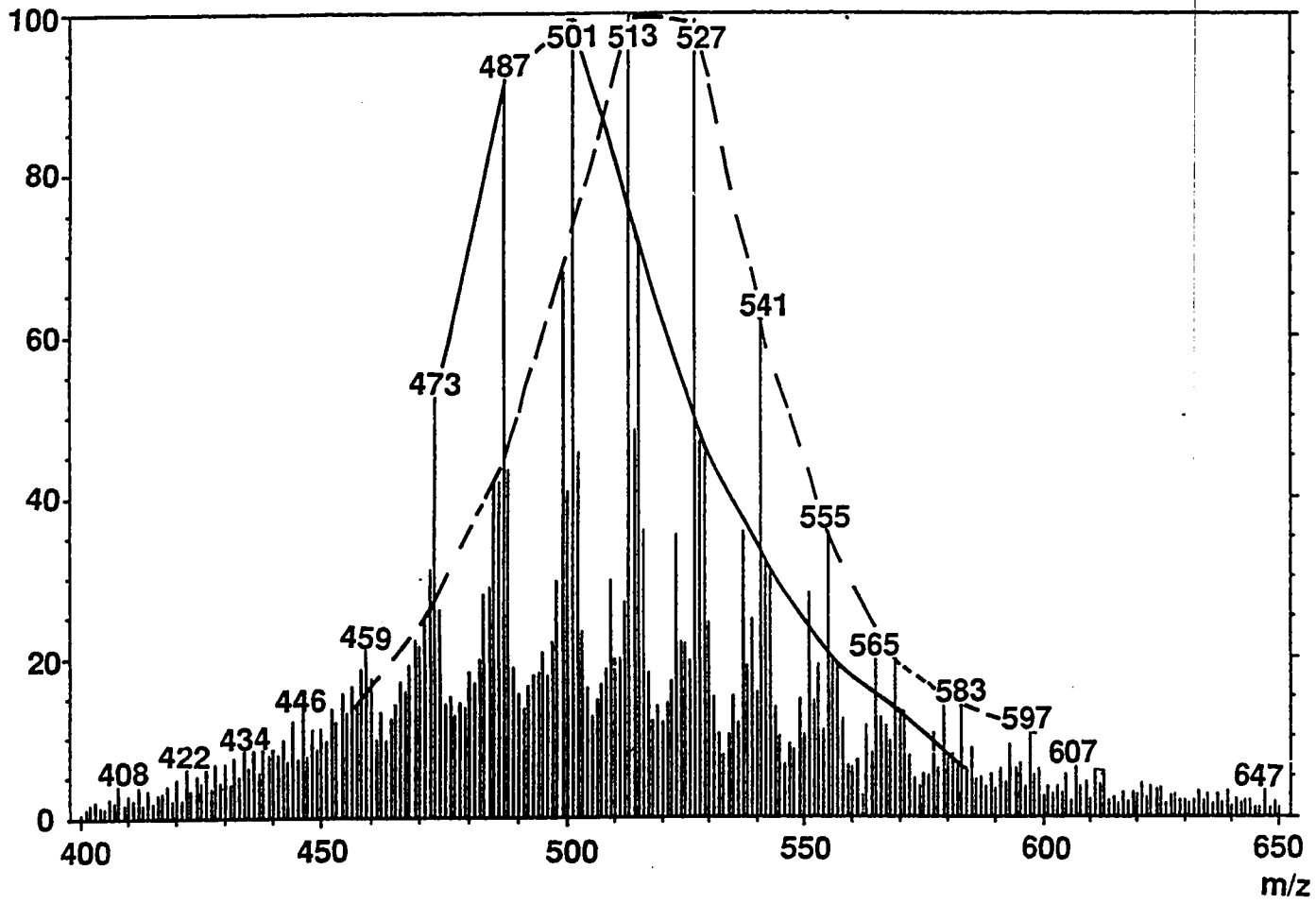


Figure (31) : EI mass spectra of vanadyl porphyrins from Arab Heavy asphaltenes ———— etio, ---------- DPEP.

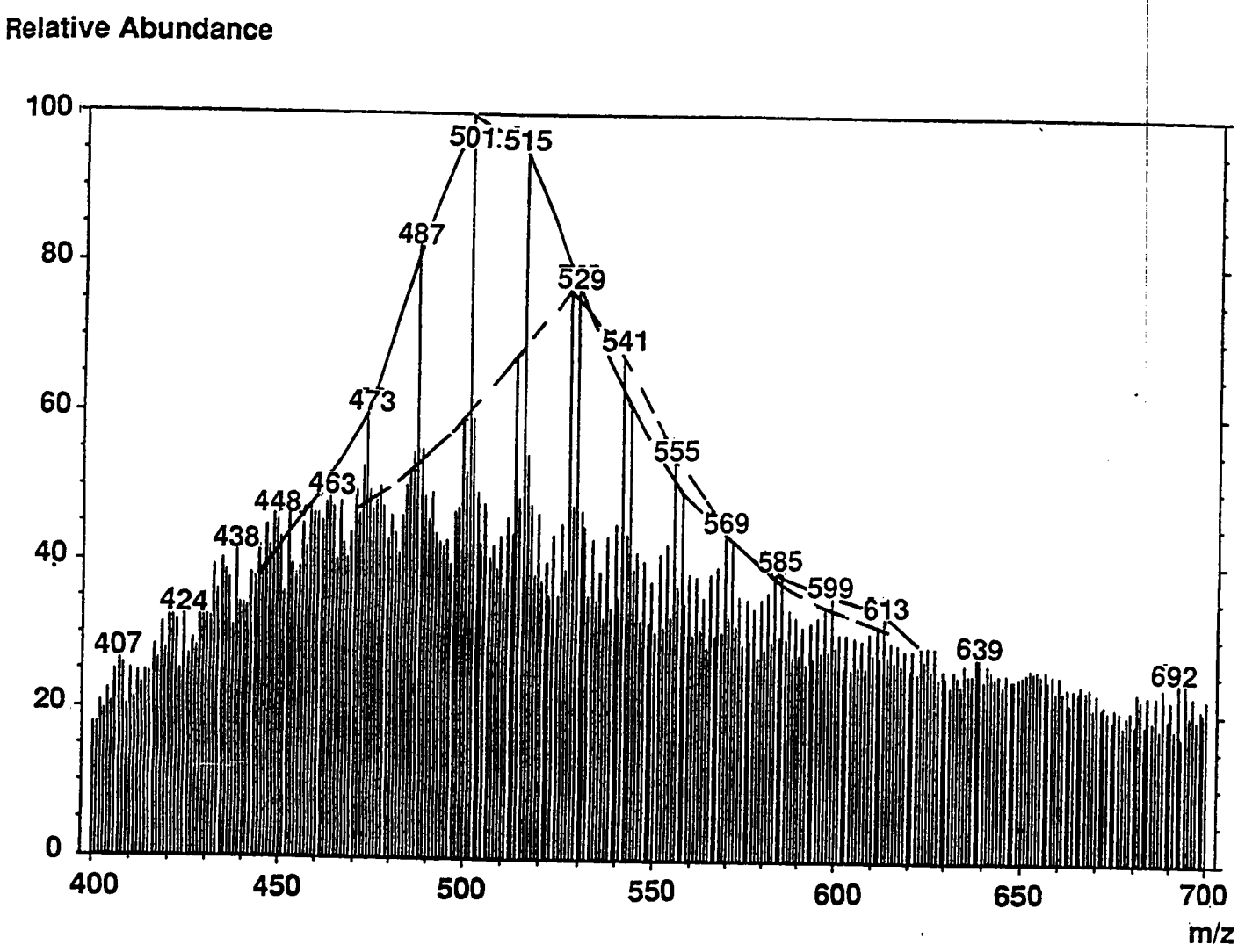


Figure (32) : EI mass spectra of vanadyl porphyrins from Arab Heavy residue
---------- DPEP and ———— etio.

series: vanadyl DPEP and etioporphyrins which agreed with Didyk et al. (64).

Asphaltenes-isolated vanadyl porphyrins were observed to consist of the series of the above two main mentioned vanadyl porphyrin types (DPEP, Etio) with carbon numbers ranging from C_{25} - C_{42} with a maximum peak at m/e 501 corresponding to C_{29} Etio. Maximum molecular peak at m/e 513 was found to correspond to C_{31} DPEP type. Where as its contents of the benzo type and the tetrahydrobenzo DPEP vanadyl type had a carbon number ranging from C_{28} - C_{42} with a maximum molecular peak at m/e 523 and 537 for C_{32} benzoetio. The benzoDPEP was found to have a carbon range of C_{28} - C_{42} with a maximum molecular peak at m/e at 493 corresponding to C_{29}. The maximum molecular peak at m/e 539 was for C_{32} tetrahydrobenzoDPEP type which was found to have a carbon range of C_{28} - C_{42}. Table 5 lists different types of vanadyl porphyrins found in the asphaltenes, their carbon range and the maximum peak for each type. Based on molecular peaks abundance, DPEP was more abundant than Etio in the asphaltenes.

The vanadyl porphyrins isolated from the residue of the Arabian Heavy crude were also found to contain the same types of the porphyrinic series with the same range of carbon distribution up to C_{42}. Based on the molecular peak relative abundance, porphyrins with Etio type were found to predominate. Also, it was found that benzo Etio > tetrabenzoDPEP > benzoDPEP vanadyl porphyrins. Table 6 lists the vanadyl porphyrins (found in residue) types, their carbon number range and their maximum molecular peaks. Etio

Table 5- Mass Spectrometric Data For Vanadyl Porphyrins From Asphaltenes

type*	formula	M.W. range	C_{number} Range	n	Max. peak
Etio	375+14n	403-683	C_{25}-C_{42}	5-22	501
DPEP	401+14n	401-681	C_{25}-C_{42}	3-22	513 & 527
BEtio	425+14n	425-687	C_{28}-C_{42}	4-22	523 & 537
BDPEP	423+14n	474-677	C_{28}-C_{42}	6-22	493
TBD	455+14n	483-680	C_{28}-C_{42}	2-22	539

* BEtio & BDPEP= Benzo Etio, & DPEP; TBD = TetrahydroBenzo DPEP

Table 6- Mass Spectrometric Data For Vanadyl Porphyrins From Residue

type*	formula	M.W. range	C_{number} Range	n	Max. peak
Etio	375+14n	403-683	C_{25}-C_{42}	5-22	501
DPEP	401+14n	429-681	C_{25}-C_{42}	3-22	527
BEtio	425+14n	453-677	C_{28}-C_{42}	4-22	495
BDPEP	423+14n	465-675	C_{27}-C_{42}	2-22	521
TBD	455+14n	483-680	C_{28}-C_{42}	2-22	553

* BEtio & BDPEP= Benzo Etio, & DPEP; TBD = TetrahydroBenzo DPEP

had a maximum molecular peak at m/e 501 corresponding to C_{29} vanadyl etioporphyrin. DPEP had its maximum molecular peak at m/e 527 which corresponded to C_{31} DPEP vanadyl porphyrin. The most abundant molecule in the homologous series of benzoetio vanadyl porphyrin was found to be C_{29} whereas C_{31} was predominant in the homologous series of benzoDPEP series. Tetrahydrobenzo vanadyl porphyrins homologous series had its maximum molecular peak at m/e 553 coressponding to C_{34}.

The mass spectra of the nickel porphyrins were similarly characterized with the presence of homologous series of porphyrins. The nickel porphyrins fraction separated from the residue cut with 3:7 chloroform/n-hexane, which showed a visible absorption band at 550 nm, was further analyzed by a low voltage (18 eV) mass spectrometer. From the mass spectra only two types of nickel porphyrins could be identified: Etio and benzoDPEP (figure 33). Homologous series of Etio with a carbon number range of C_{23} - C_{36} was identified with a maximum molecular peak corresponding to C_{26}. Where as benzoDPEP type has a homologous series ranging from C_{28} - C_{36}. with a maximum molecular peak corresponding to C_{30} (see Table 7 for more details).

4.5- Electronic Absorption Spectrophotometry:

Electronic absorption spectrophotometry is a very important tool for the detection of tetrapyrrole pigments and especially the metallo- and free-base petroporphyrins. The simple usage nature of the method has made it an invaluable technique to be used by the researchers for monitoring separations,

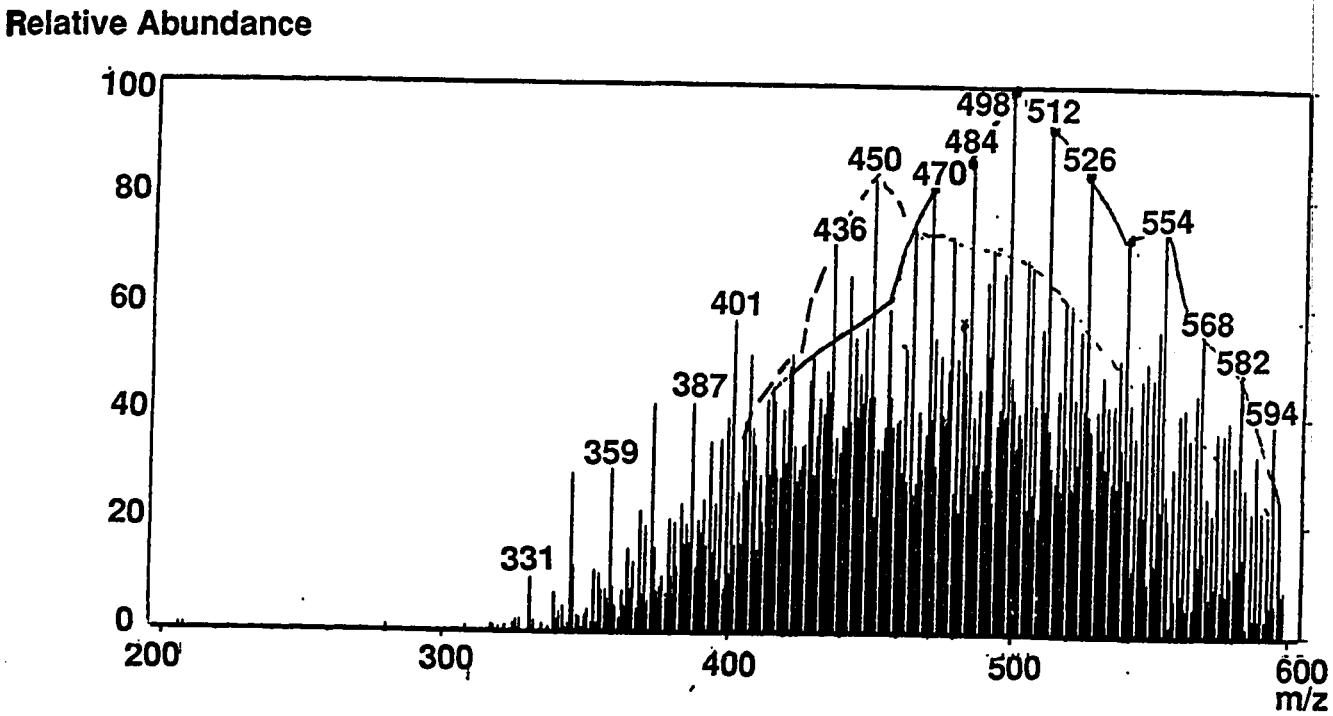


Figure (33) : EI mass spectra of nickel porphyrines:
——— Benzo DPEP, -------Etio.

Table 7- Mass Spectrometric Data For Nickel Porphyrins From Residue

type*	formula	M.W. range	C_{number} Range	n	Max. peak
Etio	366+14n	408-590	C_{23}-C_{36}	3-16	450
BDPEP	414+14n	414-596	C_{28}-C_{36}	4-16	498

* BDPEP= Benzo DPEP

elucidation of structures, and in quantitation.

The electronic spectra of the porphyrins consists of two parts: near ultraviolet and visible. The metalloporphyrins are characterized by two-banded visible spectrum and a Soret peak at ca. 400 nm. The two bands in the visible region are usually called α and β with α at higher wavelength than β. The visible absorption bands of nickel porphyrins are normally found at 550 and 514 nm and that of vanadyl porphyrins are observed at 570 and 530 nm for α and β respectively. The ratio of α/β is usually used for the classification of the metallopetroporphyrins as well as for correlation type of studies such as oil maturation study (3, 13, 14, and 55). The ratio of α/β for nickel etioporphyrins in a neutral solvent, for example, is 3 while it is 2 for nickel DPEP. The Etio vanadyl porphyrin has α/β of 2 and it is 1.3 for the vanadyl DPEP (3,13). The shift to a longer wavelength by the vanadyl porphyrin chromophore and its lower α/β ratio as compared to Etio and DPEP nickel porphyrins are due to the additional coordination with the oxygen to yield a pentacoordinated complex rather than a simple square planar nickel porphyrins

An extra absorption band is observed at still a higher wavelength making a shoulder at 590 nm is attributed to benzoporphyrins according to Baker and Louda (3).

The spectra for the vanadyl porphyrin isolated from Arabian Heavy crude residue and asphaltenes clearly showed the UV/Vis characteristic spectra at a Soret peak of 405 nm and two-banded spectra at 570 and 530 nm. There

was, however, a weak shoulder at 590 nm indicating the presence of vanadyl benzoporphyrins.

The α/β ratio was found to be equal to 1.45 and 1.70 for vanadyl porphyrins from asphaltenes and residue respectively. These two values were intermediate between the α/β values found for the vanadyl DPEP and etioporphyrins in the literature (1.3 and 2 respectively). Therefore, the α/β values of the separated vanadyl porphyrins from asphaltenes and residue indicated that the vanadyl porphyrins isolated from Arabian Heavy crude consisted of more than one type of vanadyl porphyrins (67).

CHAPTER 5

CONCLUSIONS

5.1- General:

The work reported in this thesis has significantly extended available knowledge of the separation and characterization techniques for the nickel and vanadyl porphyrins in the Arabian Heavy crude oil residue and asphaltenes. The HPLC methods developed for petroporphyrins analysis enhanced the understanding of this technique as a powerful tool for fingerprinting and laid the general work for more sophisticated studies. Major accomplishments and conclusions of this study are summerized as follows:

5.2- Separation of Nickel and Vanadyl porphyrins:

1- Not any literature reported method could be used & generalized.

2- Method should be modified taking into account nature of the sampe.

3- Extraction of the sample prior to the separation was essential.

4- Dual use of the silica gel and alumina columns proved satisfactoy.

5- TLC (silica gel) was effective tool for the final purification.

7- Separation of the vanadyl porphyrins was more satisfactory than nickel porphrins.

5.3- High Performance Liquid Chromatography Fingerprinting:

1- Satisfactory for separation of compounds and/or isomers.

2- Needed supplementary instruments and/or coinjecting standards fo

structure and/or type elucidation.

3- Minimum column length of 50 cm was satisfactory to give acceptabe separation.

4- Solvent system should be carefully chosen to optimize separation

5- Methanol was found to be a satisfactory eluent at 1ml/min.

6- Etio(III) Vanadyl standard eluted within the retention time profe of the isolated vanadyl porphyrins.

5.4- Identification Methods:

5.4.1- Ultraviolet/Visible Spectrophotometry:

UV/Vis spectrophotometry is a powerful tool for metalloporphyrins charaterization. Two banded spectra at 530 and 570 nm and a Soret band at ca. 410 nm for vanadyl Etio and DPEP were found. Another band at 590 nm for the benzo vanadyl porphyrins was observed. Absorption at 550 nm for nickel porphyrins was also observed. The α/β value was found to be intermediate between the values of Etio and DPEP standard compounds indicating that vanadyl porphyrins from residue and asphaltenes contained a mixture of both Etio & DPEP.

5.4.2- Mass Sepectrometry:

Low resolution and low voltage electron impact proved satisfactorfor the determination of:

a- Types of vanadyl porphyrins.

b- Homologous series within each type.

Types of Vanadyl porphyrins found in Arabian Heavy Crude Oil:

1- Homologous series of vanadyl porphyrins up to CH_2 found in residue and asphaltenes were of the following types: of:

- Etio
- DPEP
- Benzo Etio & DPEP
- Tetrahydrobenzo DPEP

2- Homologous series of nickel porphyrins up to C_{36} found in the residue were of the following types:

- Etio
- Benzo DPEP

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